Ion-Beam-Induced Desorption as a Method for Probing the Stability of the Molecule-Substrate Interface in Self-Assembled Monolayers

Sabina Wyczawska,^[a] Piotr Cyganik,^{*,[b]} Andreas Terfort,^[c] and Peter Lievens^{*,[a]}

During recent years self-assembled monolayers (SAMs) have been recognized as model structures for different areas in nanotechnology, ranging from nanolithography and molecular electronics to sensors and biocompatible materials.^[1] A growing range of possible new SAM applications demands better understanding of their detailed molecular structure, which is a result of balancing molecule–molecule and molecule–substrate interactions in the monolayer. Despite the numerous structural studies of SAMs available nowadays, the structure and stability of the SAM–substrate interface is still poorly understood. Even for a most simple SAM system of methanethiol on Au(111), identification of the adsorption geometry (the Au–S interface) remains controversial.^[2,3] As a consequence, the experimental and theoretical analysis of the bonding geometry and the stability of the molecule–substrate interface for technologically relevant, and therefore more complicated SAMs, is extremely difficult. Importantly, this missing information remains fundamental for most of SAMs potential applications with molecular electronics in particular.^[4]

Herein we propose using ion-induced desorption in combination with neutral fragment mass spectrometry as a method to analyze the chemical stability of the molecule–substrate interface in complicated and technologically relevant SAMs. This work builds on previous studies analyzing the behavior of SAMs on a Au(111) substrate upon bombardment with beams of Ar⁺ ions in the keV range.^[5–8] It was shown that the bombardment of aromatic thiol SAMs on a Au(111) substrate results in the ejection of neutral molecular fragments via two distinct desorption mechanisms. A minor percentage of the SAM fragments leave the surface with high kinetic energy (~eV) as a result of the direct momentum transfer from the collision cascade developed in the substrate upon primary ion impact. The overwhelming majority of desorbing particles leaves the surface with low kinetic energies (~10^{–2} eV) as a result of “gentle” cleavage of chemical bonds (with no significant momentum transfer) within the organic layer by chemical reactions initiated

by reactive fragments (e.g. radicals) created in the organic film as a result of the primary ion impact.

Following these findings, ion-induced desorption experiments were performed for aromatic SAMs that form different structural phases on the Au(111) surface.^[9] These experiments unambiguously demonstrated that the ion-induced cleavage of chemical bonds in SAMs is extremely sensitive to details of their geometric and electronic configuration, due to the chemical reaction mechanisms involved. To further investigate this effect, a homologue series of 4,4'-biphenyl-substituted alkane-thiols [CH₃–C₆H₄–C₆H₄–(CH₂)_n–SH; BPnS; *n* = 1–6] deposited on a Au(111) substrate was analyzed.^[10] Former microscopic^[11] and spectroscopic^[12,13] experiments demonstrated that, depending on the parity of the number of CH₂ units (the parameter *n* is odd or even), two different structures of BPnS/Au(111) SAMs are observed, with higher packing density and more uprightly oriented molecules for the odd-numbered systems. Importantly, this odd–even structural effect coincides with the odd–even effects reported for the stability of these SAMs towards electrochemical desorption,^[14,15] exchange by other molecules,^[16,17] electron irradiation,^[18] and thermally induced phase transitions.^[19–21] In all these different aspects of the film stability, the odd-numbered systems were more stable than the even ones. Recent ion-induced desorption experiments for the BPnS/Au(111) series demonstrated that the emission of the complete parent molecule, resulting from the Au–S bond scission and the emission of the desulfurized parent molecule ([BPnS–S]), resulting from the S–C bond scission, also exhibit clear odd–even effects.^[10] In this case, the odd BPnS/Au(111) SAMs show a systematically lower probability of the Au–S bond scission with at the same time higher probability of the S–C bond scission. Considering that the Au–S bond has to be cleaved to allow for electrochemical desorption or for exchange by other molecules capable of SAM formation, previous electrochemical^[14,15] and exchange experiments^[16,17] indicated a higher chemical stability of this bond for odd systems. If this correlation holds, one could relate efficiency of ion-induced bond scission and chemical stability of the respective bond, as was suggested recently.^[10]

However, it is known that the odd–even effect in BPnS/Au(111) SAMs changes the packing density of the molecules and thus also the molecule–molecule interaction, which must significantly influence the electrochemical desorption and molecule exchange processes. Therefore, previous desorption experiments for BPnS/Au(111) SAMs alone could not unambiguously prove the direct relation between the efficiency of the ion-induced desorption process and the chemical stability of the corresponding chemical bond at the SAM–substrate interface. Such proof could be obtained by comparing desorption

[a] Dr. S. Wyczawska, Prof. P. Lievens
Laboratory of Solid State Physics and Magnetism
Katholieke Universiteit Leuven K.U. Leuven
Celestijnenlaan 200D, 3001 Leuven (Belgium)
E-mail: Peter.Lievens@fys.kuleuven.be

[b] Dr. P. Cyganik
Smoluchowski Institute of Physics
Jagiellonian University
Reymonta 4, 30-059 Krakow (Poland)
E-mail: piotr.cyganik@uj.edu.pl

[c] Prof. A. Terfort
Institute of Inorganic and Analytical Chemistry
Goethe University, Max-von Laue-Str. 7
60438 Frankfurt am Main (Germany)

processes for SAMs in which the only difference in the energetics is related to the stability at the SAM–substrate interface. It would of course be desirable to perform such an analysis not only for a single analogue pair but for a whole family of molecules. Such an opportunity is provided by the homologue series of BPnSe/Au(111) ($n=2-6$), which are selenolate analogs ($S \rightarrow Se$ substitution) of the BPnS/Au(111) SAMs (see Figure 1).

Figure 1. Schematic structure of the BPnSe/Au(111) SAMs with indicated chemical bonds that need to be cleaved for the emission of the parent molecule (BPnSe), the deselenized parent molecule ([BPnSe–Se]), and fragments corresponding to $m/z=91$, 168 and 181.

Previous microscopic^[22] and spectroscopic^[23,24] experiments confirmed that the packing density and structure of the BPnSe/Au(111) SAMs is essentially the same as for their thiol analogs. Following this similarity, recent exchange experiments comparing BPnS/Au(111) and BPnSe/Au(111) SAMs unambiguously demonstrated higher stability of the Au–Se bond as compared to the Au–S bond in these SAMs.^[17]

The mass spectra of photoionized neutral particles emitted with low kinetic energies ($\sim 10^{-2}$ meV) following 15 keV Ar^+ ion beam bombardment of BPnSe/Au(111) SAMs ($n=2-6$) are presented in Figures 2b–f. Several molecular fragments that are common to all the spectra shown in Figure 2 are indicated in Figure 1 and correspond to the deselenized parent molecule

Figure 2. Mass spectra obtained from photoionization of neutral molecular fragments with low kinetic energy desorbed during the Ar^+ irradiation of BPnSe/Au(111) SAMs. a) $n=2$, b) $n=3$, c) $n=4$, d) $n=5$, e) $n=6$.

([BPnSe–Se]) and smaller fragments with $m/z=91$, 168, 181. For the present analysis, only two kinds of ions are of importance, namely the parent molecule (BPnSe) and the deselenized fragment of the parent molecule ([BPnSe–Se]). To compare the relative emission from different SAMs we have normalized the obtained mass abundances using the total detected amount of desorbed molecular material in the given spectra. The corresponding data are shown in Figure 3. To allow for direct comparison between BPnSe/Au(111) and BPnS/Au(111) SAMs, data obtained for [BPnSe–Se] and BPnSe emission (Figures 3a,b) are confronted with the respective data obtained earlier^[10] for [BPnS–S] and BPnS emission (Figures 3d,e).

The most striking feature of the data obtained in the present experiment is the complete absence of parent molecule (BPnSe) emission in all spectra obtained for BPnSe/Au(111) SAMs. In contrast, parent molecule emission was observed in BPnS/Au(111) SAMs desorption, exhibiting a clear odd–even oscillation.^[10] This result shows that the probability of the ion induced Au–Se bond scission must be radically lower compared to the Au–S bond. Since recent exchange experiments^[17] demonstrated that the stability of the Au–Se bond in these SAMs is higher compared to the Au–S bond, we can now directly correlate the stability of the given chemical bond at the SAM–substrate interface towards ion-induced desorption with the chemical stability of this bond.

The second feature clearly visible in Figure 3a is the odd–even effect in the emission of the deselenized fragment [BPnSe–Se]. This effect is similar to what was observed earlier^[10] for [BPnS–S] emission (compare Figures 3a,d). This observation again is fully consistent with previous experiments revealing: 1) the same character of the odd–even structural effect in both types of homologue series,^[22–24] and 2) the same odd–even character in the stability for BPnSe/Au(111) and BPnS/Au(111) SAMs against the exchange by alkaneselenols

Figure 3. The normalized photoion signals for a) the BPnSe–Se fragments, b) the parent molecules (BPnSe), and c) the total detected signal plotted as function of the number of methylene units in BPnSe/Au(111) SAMs (a–c). To enable direct comparison, respective data reported by us previously (ref. [10]) for BPnS/Au(111) SAMs are presented in (d–f). Data in (a), (b), (d) and (e) are normalized to the total detected signal. Data in (c) and (f) are normalized to the maximal value.

and alkanethiols, respectively (see Figure 5 in ref. [17]). Considering the present results, we can also directly conclude that the opposite sign of the odd–even effect for the [BPnS–S] emission as compared to BPnS (see Figures 3d,e) reflects that the increased chemical stability of the Au–S bond results in decreased stability of the S–C bond and vice versa. This is an expected chemical effect considering that the same S atom is involved in both bonds which, apparently, can be traced by our desorption experiments.

The third feature is the odd–even effect in the total photo-ion signal detected for both homologue series (Figures 2c,f). In both cases the odd–even oscillation decays with increasing number n . This effect was also observed in corresponding exchange experiments and is fully consistent with the structural model of BPnS(Se)/Au(111) SAMs as discussed earlier.^[17] The opposite phase of this oscillation in desorption for BPnSe/Au(111) and BPnS/Au(111) SAMs is directly related to the phase of the odd–even oscillation of the dominant contribution to the total photo-ion signal which comes from the deselenized parent molecule ([BPnSe–Se]) for BPnSe/Au(111), and the parent molecule (BPnS) for BPnS/Au(111) SAMs.

Thermal desorption spectroscopy (TDS) has been used to probe the relative stability of the Au–S and Au–Se bonding in SAMs. The TDS experiments conducted by Witte et al.^[25] comparing benzenethiol (BS) and benzeneselenol (BSe) on Au(111) were interpreted by the authors as indicating higher stability of the Au–S bond. However, this conclusion contradicts those of two other publications analyzing the stability of the same SAMs by competitive adsorption^[26] and electrochemical desorption.^[27] In our opinion the relative stability of the Au–S and Au–Se bonds can be compared only for thiol and selenol SAMs analogs that form the same or very similar structures. Since the packing density of BS and BSe on Au(111) is different by about 35%,^[25] such an analysis is not conclusive. More recently, however, Witte et al. have conducted TDS experiments^[28] for anthracenethiol (AntS) and anthraceneselenol (AntSe) SAMs on Au(111) (see Figure S2 in the Supporting Information of ref. [28]), which have similar packing density and structure.^[28,29] Here the TDS data show no emission of the complete AntSe molecule from AntSe/Au(111) SAMs in the investigated temperature range (350–700 K) while deselenized fragment emission is observed with a peak at 478 K.^[28] For AntS/Au(111), however, emission of the complete AntS molecule at 488 K (from the high-density phase) and the desulfurized fragment at 531 K (from the low-density flat-lying phase) was reported.^[28,29] These data (restricted to high-density phases for which such a comparison is possible) may indicate stronger Au–Se bonding as compared to the Au–S in these SAMs, which results in the emission of a deselenized fragment of the AntSe molecule (with Se atoms remaining on the surface as confirmed additionally by the XPS data)^[28] for AntSe/Au(111) and the emission of a complete AntS molecule for AntS/Au(111) SAMs in a similar temperature range. Such interpretation of TDS data obtained for AntS(Se)/Au(111) SAMs^[28,29] is consistent with desorption data shown herein, and in variance with the conclusions from the TDS data published in ref. [25].

In conclusion, our experiments unambiguously show that mass spectrometry of neutral fragments desorbed by ion bombardment of SAMs directly probes the chemical stability of the molecule–substrate interface in SAMs. Moreover, this new information together with the corresponding interpretation of the data obtained in a number of previous experiments, proves that the method proposed herein can qualitatively monitor changes in the stability of the molecule–substrate interface governed by three different aspects: 1) modification in the SAMs anchoring group (S→Se substitution, present data), 2) modifications in the chemical structure of the SAMs molecular backbone (the odd–even effects in BPnSe/Au(111) and BPnS/Au(111) SAMs, present data and ref. [10]), and 3) modifications in the surface molecular packing for a given SAM (different structural phases in even BPnS/Au(111) SAMs, ref. [10]).

This qualitative information on molecule–substrate interface energetics should in turn enhance rational design and theoretical modeling of complicated and technologically relevant SAMs. For instance BPnS/Au(111) SAMs have been the subject of recent DFT calculations analyzing both bonding geometry^[30] and electronic structure^[31] at the molecule–metal interface, not revealing, however, any odd–even effect in the Au–S bond stability visible in our desorption experiments. Also, relative stability of the Au–S and Au–Se bonding in SAMs as described herein was recently for the first time approached by DFT calculations,^[32] leading the authors to the general conclusion of a marginal difference in the stability. This is in contrast with desorption data presented herein, recent exchange experiments,^[17] and most of previous^[26,27,33,34] experimental findings. Therefore, we believe that the experimental results obtained for a well-characterized homologue series of BPnSe/Au(111) and BPnS/Au(111) SAMs could be used as a reference for selecting an appropriate theoretical approach to model SAM–substrate interface energetics.

Finally, we note that in the presented method, chemical reactions of reactive molecular fragments produced by the primary ion impact probe the chemical stability of the molecule–substrate bonding in SAMs. Since a low dose of primary ions ($\sim 10^{10}$ ions/cm², see the Experimental Section) is used for this analysis (static conditions), and the produced reactive species quickly move out of the primary ion impact zone,^[8] the proposed method analyzes, fast and locally, the unperturbed structure of the molecule–substrate interface in SAMs. This is in contrast to relatively slow thermal or electrochemical desorption experiments where, due to the global temperature^[19–21,29,35] or potential^[36] ramping, respectively, the molecule–substrate interface in SAMs can reconstruct before the desorption process takes place.

Experimental Section

BPnSe/Au(111) SAMs were formed by immersing gold-coated substrates in a 0.1 mM ethanolic solution of the corresponding diselenide [BPnSe–SeBPn: $\text{CH}_3(\text{C}_6\text{H}_4)_2(\text{CH}_2)_n\text{Se–Se}(\text{CH}_2)_n(\text{C}_6\text{H}_4)_2\text{CH}_3$ with $n=2\text{--}6$] for at least 24 h. The synthesis of the molecules is described elsewhere.^[37] After incubation all samples were rinsed with ethanol and dried in a nitrogen flow. Atomically flat Au(111) sub-

strates were epitaxially grown by thermal evaporation on air-cleaved mica.^[38] The ion-irradiation experiments were performed in a UHV laser ionization mass spectrometer. Detailed information about the setup is available elsewhere.^[39] In brief, the experimental setup consists of an UHV chamber (base pressure below 2×10^{-10} hPa), with an ion source and a time-of-flight mass spectrometer connected to it. Desorption was induced by a pulsed (500 ns) Ar^+ ion beam (15 keV) directed onto the sample surface at an incidence angle of 45° . The experiments were performed in the static regime with a total ion fluence of about 8×10^{10} ions/cm². Laser post-ionization in combination with mass spectrometry was applied to ionize and detect neutral molecular fragments. The cloud of desorbed particles was intersected at a fixed distance of 4 mm parallel to the sample surface by a focused, pulsed (6 ns, 10 Hz) laser beam delivered by an optical parametric oscillator (Quanta-Ray MOPO-730) which was pumped by a Nd:YAG laser (Spectra Physics GCR-230). In order to reduce the photofragmentation process, resonance enhanced multi-photon ionization (REMPI) was used. To ionize the phenyl-containing molecular particles, resonant two-photon one-colour photoionization was used at 259 nm with relatively low photon fluence ($\sim 10^{18}$ photons/cm²).^[40] The created photoions were subsequently accelerated and detected in a linear time-of-flight mass spectrometer with a mass resolution of about 200. Changing the delay time between the incidence of the primary ion beam pulse on the sample and the firing moment of the laser, kept at a fixed position above the sample surface, enables selection of the kinetic energy of the analyzed species. To acquire mass spectra that result from ion-induced desorption by a chemical reactions mechanism, only low-energy molecular species were analyzed in the present experiments. Note that not all observed molecular fragments exactly correspond to a given m/z value. Since small variations due to the mass calibration error can be safely excluded, we attribute the observed spread/deviation to the capture or loss of one or several protons during the desorption and/or the photoionization processes.

Acknowledgements

This work is financially supported by the Belgian Fund for Scientific Research, Flanders (FWO), the Flemish Concerted Action (GOA), Interuniversity Poles of Attraction (IAP) Research Programs, and the Polish Ministry of Science and Higher Education (0061/B/H03/2008/34). P.C. acknowledges support received from the Foundation for Polish Science under Homing fellowship.

Keywords: laser chemistry • mass spectrometry • monolayers • selenium • self-assembly

- [1] J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, *Chem. Rev.* **2005**, *105*, 1103–1170.
- [2] C. Vericat, M. E. Vela, G. Benitez, P. Carro, R. C. Salvarezza, *Chem. Soc. Rev.* **2010**, *39*, 1805–1834.
- [3] P. Maksymovych, O. Voznyy, D. B. Dougherty, D. C. Sorescu, J. T. Yates, *Prog. Surf. Sci.* **2010**, *85*, 206–240.
- [4] R. L. McCreery, A. J. Berggren, *Adv. Mater.* **2009**, *21*, 4303–4322.
- [5] D. E. Riederer, R. Chatterjee, S. W. Rosencrance, Z. Postawa, T. D. Dunbar, D. L. Allara, N. Winograd, *J. Am. Chem. Soc.* **1997**, *119*, 8089–8094.
- [6] Z. Postawa, C. A. Meserole, P. Cyganik, J. Szymonska, N. Winograd, *Nucl. Instrum. Methods Phys. Res. Sect. B* **2001**, *182*, 148–154.

- [7] E. Vandeweert, J. Bastiaansen, F. Verveacke, P. Lievens, R. E. Silverans, P. Cyganik, Z. Postawa, H. T. Rong, M. Buck, *Appl. Phys. Lett.* **2003**, *82*, 1114–1116.
- [8] P. Cyganik, E. Vandeweert, Z. Postawa, J. Bastiaansen, F. Verveacke, P. Lievens, R. E. Silverans, N. Winograd, *J. Phys. Chem. B* **2005**, *109*, 5085–5094.
- [9] F. Verveacke, S. Wyczawska, P. Cyganik, Z. Postawa, M. Buck, R. E. Silverans, P. Lievens, E. Vandeweert, *J. Phys. Chem. C* **2008**, *112*, 2248–2251.
- [10] F. Verveacke, S. Wyczawska, P. Cyganik, J. Bastiaansen, Z. Postawa, R. E. Silverans, E. Vandeweert, P. Lievens, *ChemPhysChem* **2011**, *12*, 140–144.
- [11] P. Cyganik, M. Buck, W. Azzam, C. Wöll, *J. Phys. Chem. B* **2004**, *108*, 4989–4969.
- [12] K. Heister, H. T. Rong, M. Buck, M. Zharnikov, M. Grunze, L. S. O. Johansson, *J. Phys. Chem. B* **2001**, *105*, 6888–6894.
- [13] H. T. Rong, S. Frey, Y. J. Yang, M. Zharnikov, M. Buck, M. Wünn, C. Wöll, G. Helmchen, *Langmuir* **2001**, *17*, 1582–1593.
- [14] Y. T. Long, H. T. Rong, M. Buck, M. Grunze, *J. Electroanal. Chem.* **2002**, *524*, 62–67.
- [15] I. Thom, M. Buck, *Surf. Sci.* **2005**, *581*, 33–46.
- [16] T. Felgenhauer, H. T. Rong, M. Buck, *J. Electroanal. Chem.* **2003**, *550*, 309–319.
- [17] K. Szelągowska-Kunstman, P. Cyganik, B. Schüpbach, A. Terfort, *Phys. Chem. Chem. Phys.* **2010**, *12*, 4400–4406.
- [18] S. Frey, H. T. Rong, K. Heister, Y. J. Yang, M. Buck, M. Zharnikov, *Langmuir* **2002**, *18*, 3142–3150.
- [19] P. Cyganik, M. Buck, *J. Am. Chem. Soc.* **2004**, *126*, 5960–5961.
- [20] P. Cyganik, M. Buck, T. Strunskus, A. Shaporenko, J. D. T. E. Wilton-Ely, M. Zharnikov, C. Wöll, *J. Am. Chem. Sci.* **2006**, *128*, 13868–13878.
- [21] P. Cyganik, M. Buck, T. Strunskus, A. Shaporenko, G. Witte, M. Zharnikov, C. Wöll, *J. Phys. Chem. C* **2007**, *111*, 16909–16919.
- [22] P. Cyganik, K. Szelągowska-Kunstman, A. Terfort, M. Zharnikov, *J. Phys. Chem. C* **2008**, *112*, 15466–15473.
- [23] A. Shaporenko, J. Müller, T. Weidner, A. Terfort, M. Zharnikov, *J. Am. Chem. Soc.* **2007**, *129*, 2232–2233.
- [24] T. Weidner, A. Shaporenko, J. Müller, T. Schmid, P. Cyganik, A. Terfort, M. Zharnikov, *J. Phys. Chem. C* **2008**, *112*, 12495–12506.
- [25] D. Käfer, A. Bashir, G. Witte, *J. Phys. Chem. C* **2007**, *111*, 10546–10551.
- [26] F. K. Huang, R. C. Horton, D. C. Myles, R. L. Garrell, *Langmuir* **1998**, *14*, 4802–4808.
- [27] Y. Sato, F. Mizutani, *Phys. Chem. Chem. Phys.* **2004**, *6*, 1328–1331.
- [28] A. Bashir, D. Käfer, J. Müller, C. Wöll, A. Terfort, G. Witte, *Ang. Chem. Int. Ed.* **2008**, *47*, 5250–5252.
- [29] D. Käfer, G. Witte, P. Cyganik, A. Terfort, C. Wöll, *J. Am. Chem. Soc.* **2006**, *128*, 1723–1732.
- [30] G. Heimel, L. Romaner, J. Bredas, E. Zojer, *Langmuir* **2008**, *24*, 474–482.
- [31] G. Heimel, L. Romaner, E. Zojer, J. Bredas, *Accounts Chem. Res.* **2008**, *41*, 721–729.
- [32] E. de La Llave, D. A. Scherlis, *Langmuir* **2010**, *26*, 173–178.
- [33] C. K. Yee, A. Ulman, J. D. Ruiz, A. Parikh, H. White, M. Rafailovich, *Langmuir* **2003**, *19*, 9450–9458.
- [34] T. Weidner, A. Shaporenko, J. Müller, M. Hölting, A. Terfort, M. Zharnikov, *J. Phys. Chem. C* **2007**, *111*, 11627–11635.
- [35] P. Cyganik, M. Buck, J. D. T. E. Wilton-Ely, C. Wöll, *J. Phys. Chem. B* **2005**, *109*, 10902–10908.
- [36] V. Mirsky, *Trends in Analytical Chemistry* **2002**, *21*, 439–450.
- [37] J. Müller, A. Terfort, *Inorg. Chim. Acta* **2006**, *359*, 4821–4827.
- [38] N. Vandamme, G. Verschoren, A. Depuydt, M. Cannaeys, W. Bouwen, P. Lievens, R. E. Silverans, C. Van Haesendonck, *Appl. Phys. A* **2001**, *72*, S177.
- [39] E. Vandeweert, P. Lievens, V. Philipsen, J. Bastiaansen, R. E. Silverans, *Phys. Rev. B* **2001**, *64*, 195417.
- [40] E. Vandeweert, C. A. Meserole, A. Sosteracz, Y. Dou, N. Winograd, Z. Postawa, *Nucl. Instrum. Methods Phys. Res. Sect. B* **2000**, *164–165*, 820–826.

Received: July 8, 2011

Published online on August 25, 2011