Relative Stability of Thiolate and Selenolate SAMs on Ag(111) Substrate Studied by Static SIMS. Oscillation in Stability of Consecutive Chemical Bonds

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ABSTRACT: The stability of chemical bonds at the molecule–metal interface is of fundamental importance for a majority of applications based on organic materials. It remains, however, extremely difficult to determine this stability using experimental and theoretical methods. A detailed analysis of the static SIMS (S-SIMS) data obtained for the homologous series of thiolate- and selenolate-based self-assembled monolayers (SAMs) on the Ag(111) substrate reveals positional oscillations in the stability of consecutive chemical bonds in the vicinity of the molecule–metal interface. The observed oscillations are much more pronounced compared to recently reported analogous data for the Au(111) substrate, which confirms the universal nature of this phenomenon and its strong dependence on the type of molecule binding atom (S or Se) and the substrate (Ag or Au). Importantly, such an analysis has not been conducted to date using any other technique, and this study not only reveals the universal mechanisms of molecule–metal interface stability but also presents S-SIMS as a unique tool for such an analysis.

1. INTRODUCTION

Self-assembled monolayers (SAMs)† currently play a key role in many aspects of surface and thin film design, which is related to further progress in different areas of nanotechnology, ranging from patterned materials1−10 and molecular electronics11−16 to biocompatible17−20 materials. To our knowledge, the most basic parameter in the design of SAMs is the stability of their chemical bonding with selected substrates. Unfortunately, it remains extremely difficult to determine this parameter using both experimental analysis and theoretical predictions, which thus limits our efforts in the purposeful design of SAMs. Therefore, new experimental approaches for exploring the molecule–substrate interface stability are urgently required to provide systematic and general observations, which could in turn enable the development of theoretical models. In this work, we demonstrate that static secondary ion mass spectrometry (S-SIMS) can play such a role by not only providing an alternative method for conducting typical stability experiments but, more importantly, revealing and exploring the stability mechanisms which to date has not been analyzed by any other technique. Over the last 3 decades, S-SIMS has emerged as one of the fundamental surface and elemental characterization tools to study the composition and reactivity, and more recently, for the imaging of organic films and biological structures.12−17 An extremely high sensitivity, which enables the trace analysis of the chemical composition down to the ppb level, is one of the key features that make S-SIMS particularly attractive for many applications. Among organic films, SAMs are considered as model systems for S-SIMS analysis from both the experimental and calculation viewpoint.18−28 To address the issue of the S-SIMS sensitivity to the stability of the molecule–metal interface, we have selected a homologous series of hybrid aromatic/aliphatic SAMs in the general form of CH3−(C6H4)n−2C6H4−S(Se)−Ag (n = 2−6), where either the S atom (BPnS) or Se atom (BPnSe) acts as a headgroup binding molecule to the Ag(111) surface (see Figure 1). Previous spectroscopic29−33 and microscopic34−36 measurements demonstrated that BPnS/Se molecules form very well-defined SAMs on Au(111) and Ag(111) substrates, which can be considered model systems for systematic studies. In contrast to simple alkanethiols,3 the structure of this type of SAMs depends strictly on the parity of the parameter n (the number of CH2 groups). For the Au(111) substrate, this odd−even effect results in a higher packing density of more upright oriented molecules for odd-numbered members of the BPnS(Se)/Au series. In contrast, for the Ag(111) substrate, this odd−even effect is reversed as a consequence of the different value of the substrate-S(Se)-C bond angle that is preferred for the Au(111) and Ag(111) substrates and amounts to ∼104° and ∼180°, respectively.30−33 The impact of this odd−even effect on film stability has only been analyzed for the Au(111) substrate. It was shown that the odd−even effect influences the stability of BPnS/Au SAMs toward electro-
chemical desorption, ion-induced desorption, exchange by other molecules, electron irradiation and thermally induced phase transitions. For all of these odd—even effects, with respect to the different aspects of film stability, the even-numbered members turn out to be less stable than the odd-numbered BPnSe/Au SAMs. However, for the Au(111) substrate, it was also demonstrated that the substitution of the headgroup atom from S to Se has an even more pronounced effect. Previous exchange experiments demonstrated a much higher stability of BPnSe/Au SAMs compared to BPnS/Au SAMs due to the stronger Se–Au bond compared to the S–Au bond. Lastly, a recent stability study for the BPnS/Au SAMs revealed the effect of positional oscillation on the stability of consecutive chemical bonds of adsorbed molecules at the molecule-Au interface. This study indicated that the strength of the chemical bonding with the Au(111) substrate via the S(Se)–Au bond influences the stability of several consecutive chemical bonds inside the chemisorbed molecule. Moreover, our most recent experiments also indicate a direct influence of this oscillation effect on the relative conductivity of thiolate and selenolate SAMs on the Au(111) substrate.

In summary, we note that, to date, the analysis of the molecule-metal interface stability for the model BPnS(Se) SAMs has only been performed for the Au(111) substrate. By current experimental study, we extend this analysis to the Ag(111) substrate and address several important issues. First, we analyze the impact of the odd—even effect on the stability of BPnS(Se)/Ag SAMs. Next, we determine the impact of S → Se substitutions on the bonding with the Ag(111) substrate. Finally, and most importantly, we analyze the impact of the Au → Ag substrate modification on the effect of positional oscillation in stability of consecutive chemical bonds to confirm the origin of this phenomenon and its universal nature. To enable the direct comparison of all the effects reported here for the Ag(111) substrate with respective data for the Au(111) substrate in a single set of experiments, we have reproduced some of the data obtained earlier for the Au(111) substrate. This combined analysis provides also some implications on the relative thermal stability and conductance of these SAMs and presents S-SIMS as a new and unique tool for the molecule-metal interface stability analysis.

2. EXPERIMENTAL PART

The Ag(111) and Au(111) substrates were prepared by evaporating 150 nm of silver/gold onto single-crystal silicon (100) wafers (ITME, Warsaw) primed with a 5 nm chromium adhesion layer (base pressure of ~10⁻⁷ mbar, rate 0.1 nm/s). The synthesis of the BPnSH \((\text{CH}_3\text{(C}_6\text{H}_4\text{)}_2\text{(CH}_2)_n\text{SH}, n = 2–6)\) molecules has been described elsewhere. The precursor molecules for the fabrication of the BPnSe SAMs were diselenides \((\text{BPnSe-SeBPn: CH}_3\text{(C}_6\text{H}_4\text{)}_2\text{(CH}_2)_n\text{Se-Se-CH}_3\text{(C}_6\text{H}_4\text{)}_2\text{CH}_3, n = 2–6),\) whose synthesis has been described elsewhere. HDT \((\text{CH}_3\text{(CH}_2)_n\text{SH})\) was used as received from Aldrich. The HDSe molecules were obtained by the reduction of a hexadecyl diselenide/triselenide mixture with lithium aluminum hydride. The BPnS(Se)/Ag(Au) SAMs were prepared by immersing the substrate (Ag or Au), directly after the evaporation process was completed, into 0.1 mM solutions of the respective precursors in ethanol at room temperature for 24 h. After immersion, the samples were rinsed with pure ethanol, blow-dried with nitrogen and immediately transferred to the experimental setup (S-SIMS or IRRAS). For exchange experiments, the BPnS(Se) SAMs were immersed in 1 mM ethanolic solutions of HDT or HDS for 24 h.

Infrared reflection-absorption spectroscopy (IRRAS) measurements were performed with a dry-air-purged Thermo Scientific Nicolet 6700 FTIR spectrometer model equipped with a liquid nitrogen-cooled MCT detector. All spectra were taken using p-polarized light incident at a fixed angle of 80° with respect to the surface normal. Spectra were measured at a resolution of 2 cm⁻¹ and are reported in absorbance units \(A = -\log R/R_0,\) where \(R\) is the reflectivity of the substrate with a monolayer and \(R_0\) is the reflectivity of the reference. Substrates covered with perdeuterated hexadecanethiolate SAMs were used as the reference samples.

The SIMS analysis was performed using a TOF SIMS V system (ION TOF GmbH, Germany). The instrument was operated at a base pressure of \(6 \times 10^{-10}\) mbar. The primary 30 keV Bi⁺ ion beam was scanned over a 500 μm × 500 μm area during data acquisition. All spectra were acquired in the static SIMS regime (S-SIMS) using a total ion dose of up to \(5 \times 10^{10}\) ions/cm², which for this type of SAM ensures an analysis with no ion-induced damage, as documented by our previous studies. The secondary positive or negative ions were extracted into a reflectron-equipped time-of-flight mass spectrometer before they reached the MCP detector. For each type of BPnS(Se)/Ag(Au) SAM, three different samples were prepared and six different areas (three for positive spectra and three for negative spectra in the range up to \(m/z = 800)\) on each sample were examined, resulting in ca. 10% reproducibility in the peak intensities. Before the analysis, all spectra were normalized to the respective total number of counts.

3. RESULTS

Two types of experiments have been performed in this study. The first experiments, which probe the relative stability of the BPnS/Ag and BPnSe/Ag SAMs toward exchange by other molecules that are capable of forming SAMs, were conducted and compared with corresponding data obtained for the Au substrate. In the second experiment, which was the primary part of this study, the ion-induced desorption of the BPnS(Se)/Ag SAMs was determined via S-SIMS analysis and compared with corresponding data obtained for the Ag substrate.
3.1. Exchange Experiments. To probe the relative stability of \( \text{S}^-\text{Ag} \) and \( \text{Se}^-\text{Ag} \) bonds in the exchange experiments, a 24 h incubation of the BP\(_n\)S/Ag and BP\(_n\)Se/Ag samples in 1 mM hexadecaneselenol (HDSe) or hexadecanethiol (HDT) ethanolic solution, respectively, was performed. The progress of the exchange reaction was monitored by IRRAS. As a reference for monitoring the exchange process, the IRRAS analysis for the native BP\(_n\)S(Se)/Ag (\( n = 2 - 6 \)) SAMs was first performed. Several absorption bands characteristic of this type of SAM could be identified, as indicated in Figure 2a, where an example of the spectrum obtained for the BP3S/Ag SAM is presented. According to previous detailed spectroscopic experiments,\(^{31,33} \) the biphenyl part of the molecules results in bands at \( \sim 3028 \) (C–H stretching), \( \sim 1500 \) (C–C stretching), and \( \sim 1005 \) cm\(^{-1} \) (C–H bending), whereas the aliphatic part is attributed to bands located at \( \sim 2920 \) (C–H asymmetric stretching) and \( \sim 2865 \) cm\(^{-1} \) (C–H symmetric stretching). The weak band observed at \( \sim 1380 \) cm\(^{-1} \) corresponds to the C–CH\(_3\) symmetric deformation at the terminal group. Following the methodology proposed in our previous study,\(^{41} \) we calculated the exchange percentage of a given BPnS(Se)/Ag SAM by taking the total intensity of the bands exclusively related to the biphenyl moiety (i.e., \( \sim 3028, \sim 1500, \) and \( \sim 1005 \) cm\(^{-1} \)) and normalizing it by the respective value obtained for the native sample. The results obtained after a 24 h incubation of BPnS/Ag (\( n = 2 - 6 \)) SAMs in a 1 mM ethanolic solution of HDSe are presented in Figure 2b and show an odd–even dependence with a higher exchange percentage for odd-numbered members of the BPnS/Ag series. In contrast, the experiments presented in Figure 2c for the corresponding BPnSe/Ag (\( n = 2 - 6 \)) SAMs exchanged in a 1 mM ethanolic solution of HDT show no exchange at all. For comparison, in Figure 2d and 2e, the corresponding experiments performed for the Au substrate show a complete exchange for the BPnS/Au SAMs and no exchange for the BPnSe/Au SAMs, which is in full agreement with our previous study.\(^{41} \)

3.2. S-SIMS Experiments. S-SIMS experiments were performed for four homologous series of BPnS(Se)/Ag(Au) SAMs with \( n = 2 - 6 \) to independently probe the impact of the headgroup atom (S or Se) and the substrate (Ag or Au) modification on the molecule–metal interface stability. First, the signal of the molecule–metal cluster ions, which are very well-known fingerprints used in the S-SIMS technique to determine the formation of SAMs,\(^{18 - 27} \) was analyzed. Such an analysis of the molecule–metal clusters ions for both
BPnS(Se)/Ag and BPnS(Se)/Au SAMs was performed for the first time. An example of the obtained data is shown in Figure 3, where the normalized signal (normalized to the total number of counts) of the negative $M_2\text{Au}^-$ and $M_2\text{Ag}^-$ secondary ions is presented. The symbol “$M$” denotes the respective molecule in the general form of $\text{CH}_2\text{(C}_6\text{H}_4\text{)}_n\text{CH}_2\text{S(Se)}$ with $n = 2-6$. The data obtained for the Ag and Au substrate are similar and exhibit two common features. First, independent of the type of substrate, the intensity of the $M_2\text{Ag}^-$ signal is about an order of magnitude higher for the $\text{S}$ headgroup (BP$n\text{S}$) compared to the corresponding $\text{Se}$ headgroup (BP$n\text{Se}$). Second, depending on the parameter $n$ for both types of substrates (Ag and Au) and headgroup atoms ($\text{S}$ and $\text{Se}$), a much weaker but visible odd—even variation of the signal intensity is observed. Importantly, the phase of these odd—even oscillations for both the $\text{S}$- and $\text{Se}$-based SAMs is reversed for the Ag and Au substrates. For the Ag substrate, a higher intensity of the $M_2\text{Ag}^-$ signal is observed for even-numbered members of the BP$n\text{S(Se)}$ series with the exception of the BP6S(Se)/Ag SAMs, for which the signal is lower than expected. This could, however, be the result of a general drop in the secondary ion signal with the increase in the mass of analyzed ion, which also explains why for the Au substrate,

Figure 3. S-SIMS data analysis. Left and right panels show the normalized signal of the $[(\text{M}_2\text{Au})^-]$ and $[(\text{M}_2\text{Ag})^-]$ emission, respectively. (a and b) Emission from BP$n\text{S(Au)}$ and BP$n\text{S(Ag)}$ SAMs, respectively (blue line). (c and d) Emission from BP$n\text{Se(Au)}$ and BP$n\text{Se(Ag)}$ SAMs, respectively (red line). See the text for more details.

Figure 4. S-SIMS data analysis. Left and right panels show data obtained for BP$n\text{S(Se)}$/Ag and BP$n\text{S(Se)}$/Au, respectively. (a and b) Normalized emission of ions related to the complete molecule $[M]^+$ emitted from BP$n\text{S(Se)}$/Ag and BP$n\text{S(Se)}$/Au, respectively. (c and d) Normalized emission of ions related to the desulfurized or deselenized molecule $[M-(\text{S/Se})]^+$ emitted from BP$n\text{S(Se)}$/Ag and BP$n\text{S(Se)}$/Au, respectively. Data obtained for the $\text{S}$ and $\text{Se}$ headgroup atoms are presented in blue and red bars, respectively. See the text for more details.
where the phase of this oscillation is reversed, the BP6S/Au and BP6Se/Au SAMs show an approximately zero intensity.

In the next step, the emission of positive ions that correspond to the complete molecule $M_{S/Se}^+$ and its desulfurized ($[M − S]^{+}$) or deselenized ($[M − Se]^{+}$) fragments was analyzed. The respective data are presented in Figure 4. For the Ag substrate, the emission of $M_{S/Se}^+$ ion has a very low intensity, but it is systematically more efficient for the S headgroup compared to the Se headgroup (Figure 4a). Corresponding data obtained for the Au substrate show a much higher level of the $M_{S/Se}^+$ ion emission compared with the Ag substrate (Figure 4b), but similar to the Ag substrate, a higher intensity of the $M_{S/Se}^+$ ion emission is observed for the S headgroup compared to the Se headgroup. The emission of the desulfurized ($[M − S]^{+}$) and deselenized ($[M − Se]^{+}$) fragments was efficient for both the Ag and Au substrates, as shown in Figures 4c and 4d, respectively. Importantly, in contrast to the data obtained for the $M_{S/Se}^+$ ion, the emission of $[M − S]^{+}$ and $[M − Se]^{+}$ ions is systematically more efficient for the Se headgroup compared to the S headgroup. Additionally, whereas for the Au substrate, only a systematic drop in the $[M − S]^{+}$ and $[M − Se]^{+}$ intensity is observed as the length of molecules (defined by the parameter $n$) increases, for the Ag substrate an odd–even variation of this signal is also observed along with a higher emission for even numbered members of the BPnS(Ag) series.

The emission of $M_{S/Se}^+$ and $[M − S(Se)]^{+}$ secondary ions results from the ion-beam induced scission of the first and the second chemical bond along the molecular chain of the adsorbed molecule, respectively. For both substrates, the emission shows a reversed relationship for the S and Se headgroup atoms; i.e., for S, a higher emission of $M_{S/Se}^+$ with a simultaneous lower emission of $[M − S(Se)]^{+}$ is observed compared to the Se analogue. In Figure 5, a broader analysis of this effect is shown by comparing the relative intensity of the secondary ions emitted from the S and Se analogues, which correspond to molecular fragments generated by the scission of one of four consecutive chemical bonds along the molecular chain; the consecutive bonds start from the headgroup atom and are numbered as bonds I−IV (as shown in the schematic cartoon in Figure 5a). The data obtained for the BPnS(Se)/Ag SAMs with $n = 2, 3, 4,$ and $5$ (the low intensity of the respective signals for $n = 6$ precludes such an analysis) are presented in Figure 5b−e. The corresponding data obtained for the BPnS(Se)/Au SAMs are presented in Figure 5f−i. We note that for $n = 4$ and $n = 5$ for the BPnS(Se)/Ag SAMs, the signal ratio for bond number I is missing (the absence of corresponding points in Figure 5d and 5e). This is due to the lack of a measurable emission level of the complete molecule in this case (see Figure 4a) and thus, a high (>1), but undefined at this point, value of the corresponding ratio of this signal for the S- and Se-based analogues.

The final data analysis step is presented in Figure 6. In panel a, the analysis of the $[C_{15}H_{15}]^{+}$ secondary ion emission from the BPnS(Se)/Ag(Au) SAMs is summarized. The schematic cartoon in this panel shows that the emission of this particular fragment from the BPnS(Se)/Ag(Au) series (with $n = 2−6$) requires the cleavage of consecutive chemical bonds along the aliphatic chain, i.e., for $n = 2$, the S(Se)-C$^1$ bond has to be cleaved, for $n = 3$ the C$^1$-C$^2$ bond has to be cleaved, etc. (the
upper indexes “1” and “2” denote the first and second C atom, respectively, of the aliphatic chain, counting from the headgroup atom attachment to the chain. The data summarized in this panel show a few extremely interesting features. First, the intensity of the \([\text{C}_{15}\text{H}_{15}]^+\) emission depends strongly on the parameter \(n\), with oscillations observed for both \(n\)...
the S and Se analogues on the Au and Ag substrates and a higher signal for even values of \( n \). Second, the same phase of these oscillations is observed for the S and Se analogues, which is also independent of the type of substrate (Ag or Au). Third, the amplitude of these oscillations for both types of substrates is higher for the Se analogues compared to the S analogues. Fourth, the oscillation amplitude rapidly diminishes as the number \( n \) increases for both types of headgroup atoms (S and Se) and substrates (Ag and Au). Fifth, the amplitude of these oscillations is systematically higher for the Ag substrate compared to the Au substrate. In panels b and c, the same analysis was performed for the \([\text{C}_{16}\text{H}_{17}]^+\) and \([\text{C}_7\text{H}_{15}]^+\) fragments, respectively. As schematically indicated in the respective cartoons, the analysis in these cases is limited to the \([\text{C}_{16}\text{H}_{17}]^+\) emission are fully reproduced in the data obtained for the \([\text{C}_7\text{H}_{15}]^+\) fragment. We note here that for the \([\text{C}_{16}\text{H}_{17}]^+\) fragment, the phase of signal oscillation with \( n \) is reversed compared to the data obtained for the \([\text{C}_7\text{H}_{15}]^+\) fragment. This is a consequence of shifting our analysis from precursors.47 For the Ag substrate, previous competitive adsorption experiments have been performed for purely aromatic SAMs based on naphthalene and phenyl rings within the monolayer and with the Ag substrate, or simply (iii) the concentration of defects in a given SAM. In contrast, the current analysis is conducted for BPnS(Se)/Ag\((n = 2–6)\) SAMs, which have been formed on well-defined Ag(111) substrates and characterized spectroscopically in detail to demonstrate a similar packing density and orientation of molecules in all the compared SAMs. Therefore, in our opinion, the presented exchange data better justifies the correlation between the observed stability differences and the relative strength of the S–Ag and Se–Ag chemical bonding in these SAMs. In particular, the stability analysis presented here is not limited to comparing only two SAMs, instead, two homologous series of analogue SAMs can be compared, which makes the related observations significantly more general.

Current exchange experiments also reveal an odd—even effect in the exchange of BPnS/Ag SAMs by HDSe molecules (Figure 2b). Although a similar effect could not be observed for the BPnS/Au SAMs exchanged by HDSe molecules due to the complete exchange observed in this case (Figure 2d), such an odd—even effect in the exchange was observed for the BPnS/Au SAMs in our previous experiments when HDT molecules were exchanged instead of HDSe molecules (see Figure 5 in ref 41). More importantly, by comparing both exchange experiments performed for the same SAMs on Ag and Au substrates, we conclude that the phase of this effect is reversed upon changing the substrate from Ag to Au. As indicated in the introduction, previous microscopic and spectroscopic characterizations of BPnS(Se)/Ag(Au) SAMs demonstrated that structural odd—even effect also reverses in phase upon changing the substrate from Ag to Au. Thus, the exchange experiment remains fully correlated with the structural odd—even effect.

For a detailed analysis of the observed differences in the stability of the SAMs at the molecule–metal interface, ion-induced desorption experiments have been performed. The emission of secondary ions measured by the S-SIMS results from a convolution of the desorption and ionization processes, which are induced by the impact of primary Bi⁺ ions. Two types of characteristic secondary ions were analyzed in our study: molecule–metal clusters and different molecular fragments.
Generally, two different mechanisms of ion-induced desorption of SAMs have been identified in previous studies.\textsuperscript{22,28,39,51–53} The first mechanism is based on the well-known collision cascade process, which develops in the substrate upon primary ion impact and leads to momentum transfer to the surface atoms of the substrate and subsequently, to the desorption of the organic monolayer. In the second so-called chemical reaction mechanism, the desorption of molecular ions is caused by a “gentle” cleavage of chemical bonds (with no significant momentum transfer) within the organic layer by chemical reactions. These reactions are initiated by the reactive fragments (e.g., radicals) created in the organic film as a result of the impact of primary ions. The experimental analysis of the kinetic energy distribution for neutral species demonstrated that majority of the molecular fragments are emitted from SAMs by the chemical reaction mechanism and only a minority by the collision cascade process.\textsuperscript{39,51–53} However, by considering the ionization process, which is essential in the emission analyzed by S-SIMS, we expect that both emission mechanisms must be considered in the emission of molecular fragments.\textsuperscript{46} In contrast, for molecule–metal clusters, the gentle chemical reaction mechanism can be excluded given the presence of metal substrate atoms in the cluster, which have to be emitted by significant momentum transfer, i.e., via the collision cascade mechanism.

We begin the discussion of the S-SIMS data with the M\textsubscript{2}Ag\textsuperscript{−} and M\textsubscript{2}Au\textsuperscript{−} secondary ions, which represent the molecule–metal cluster emission. The emission of these secondary ions is closely correlated to the exchange experiments. First, similar to the exchange experiments, it shows that the selection of the headgroup atom (S or Se) has the highest impact on the intensity of the S-SIMS signal. Specifically, an order of magnitude higher emission of M\textsubscript{2}Ag\textsuperscript{−} and M\textsubscript{2}Au\textsuperscript{−} is observed for the S headgroup atom compared to Se. This extremely strong effect in the S-SIMS data can be correlated with the zero-one effect in the exchange data, which indicate higher stability of the Se–Ag(Au) bonding compared to the S–Ag(Au). As previously indicated, we may assume that the process that leads to the emission of molecule–metal clusters is essentially directed by the collision cascade mechanism. This observation gives us some insight into possible scenarios that result in the emission of molecule–metal clusters based on the molecular dynamics (MD) calculations of the ion-induced desorption process, which are limited to ballistic collisions, i.e., electronic excitations and chemical reactions are not considered in this approach. Such MD simulations, performed for octanethiol SAMs on the Au(111) substrate and used to address the mechanism of molecule–metal cluster formation, demonstrated that M\textsubscript{2}Au clusters are formed by two neighboring molecules in the original SAM structure with an Au atom originating from the top surface layer and located in the vicinity of both molecules.\textsuperscript{51} Moreover, we note, at this point, that current structural models\textsuperscript{54–56} for the adsorption of thiols on Ag(111) and Au(111) substrates assume that two neighboring molecules bind to the same surface adatom, which directly supports the correlation between the emission of the M\textsubscript{2}Ag\textsuperscript{−} and M\textsubscript{2}Au\textsuperscript{−} ions and the original SAM structure, i.e., the molecule–metal cluster formation is directly correlated with the distance between neighboring molecules and their binding (configuration and strength) with the substrate atoms. The second and less pronounced effect that is observed in the M\textsubscript{2}Ag\textsuperscript{−} and M\textsubscript{2}Au\textsuperscript{−} emission from the BPnS(Se)/Au(Ag) SAMs is the odd–even dependence. Importantly, the phase of this effect is independent of whether S or Se is used as the headgroup atom, but it becomes reversed once the substrate is changed from the Au(111) to the Ag(111) substrate. Thus, the odd–even effect in M\textsubscript{2}Ag\textsuperscript{−} and M\textsubscript{2}Au\textsuperscript{−} emission is fully correlated to the odd–even effect in the exchange experiments and structural changes in the BPnS(Se)/Au(Ag) SAMs discussed above.

So far, we have discussed the S-SIMS data, which follow changes in the molecule–metal interface stability that were already analyzed by the exchange experiments. In the following part of our discussion, we would like to focus on the molecule–metal interface analysis, which at this moment seems exclusively possible by this technique. Our analysis follows a very recent study\textsuperscript{50} where the S-SIMS data obtained for BPnS(Se)/Au were used to detect the positional oscillations in the stability of consecutive bonds along the adsorbed molecule. By performing a similar analysis for both the Ag and Au substrates, we aimed to determine the universal nature of the model proposed by us to explain this phenomenon and probe its independence on the structural odd–even effect. The first step in this analysis involved comparing the emission of ions that correspond to the complete parent molecule (M\textsubscript{2}S/Se\textsuperscript{+}) for both types of headgroup atoms (S and Se) and substrates (Ag and Au). Our data demonstrate that for both types of substrates, the emission of M\textsubscript{2}S/Se\textsuperscript{+} is much more pronounced for the S-based monolayers than the Se analogue. Because the emission of these ions results from the ion-beam induced scission of the respective chemical bond linking molecule to the metal substrate, we conclude that irrespective of the Au or Ag substrate, such a bond scission is more efficient for the S headgroup atom. By assuming that the efficiency in terminating a particular chemical bond by ion-induced processes depends on the stability of this bond, as concluded in our recent study based on corresponding experiments, MD simulations, and DFT calculations,\textsuperscript{46} our present results indicate that the stability of the Au(Ag)-Se bond is higher than that of the Au(Ag)-S bond, in this type of SAMs. Importantly, this conclusion is fully consistent with the exchange experiments discussed above for both types of substrate and with the analysis of the M\textsubscript{2}Ag\textsuperscript{−} and M\textsubscript{2}Au\textsuperscript{−} cluster ion emission. In addition, much lower intensity of M\textsubscript{2}S/Se\textsuperscript{+} ions emission for the Ag substrate compared to Au indicates higher stability of the molecule–metal binding for the latter case.

In the next step of our analysis, the relative emission of the desulfurized [M − S]\textsuperscript{+} and deselenized [M − Se]\textsuperscript{+} fragments for both types of substrates was compared (Figure 4). Because the emission of these fragments corresponds to the scission of the S(Se)−C\textsuperscript{1} bond, the higher emission observed for the S-based monolayers on Ag and Au substrates indicates the lower stability of the Se−C\textsuperscript{1} bond compared to that of the S−C\textsuperscript{1} bond for both types of substrates. From the supporting observation of positional oscillations in the stability of chemical bonds,\textsuperscript{46} such a behavior could be attributed to the fact that valence electrons of the headgroup atom (S or Se) are involved in bonding with the substrate (Ag or Au) atom(s) on one side and with its neighboring C\textsuperscript{1} atom on the other side. The increased involvement of valence electrons of the headgroup atom in one of these chemical bonds, i.e., Au(Ag)−S(Se), should result in a lower involvement of these electrons in the second bond, which consequently reduces the stability of the S(Se)−C\textsuperscript{1} bond.

In addition to the strong impact of the S or Se headgroup atom on the relative intensity in the emission of M\textsubscript{2}S/Se\textsuperscript{+} and [M − S(Se)]\textsuperscript{+} secondary ions, as discussed above, the modification
of this signal with the odd–even change of parameter n is also visible; however, this only occurs for the Ag substrate. Such an effect is pronounced for the [M − S(Se)]+ fragment (Figure 4d) where a higher emission is observed for even numbered members of the BnPn(S(Se))/Ag series. Here, we indicate that this odd–even variation in the signal is overlaid with a rapid drop of the signal as the n value increases due to an increased mass of the respective molecule. This is the reason why the intensity for n = 6 is extremely low and out of sync with this odd–even trend. For the M$_{S/Se}^+$ ion, where the overall emission is extremely weak, this effect is much less pronounced but still visible for n = 2, 3, and 4, with the highest emission observed for n = 3, i.e., for the odd-numbered member of the BnPn(S(Se))/Ag series. Importantly, the higher emission of the M$_{S/Se}^+$ for the odd-numbered BnPn(S(Se))/Ag SAMs correlates with the respective exchange experiments that show the lower Ag−S bond stability of odd-numbered members of the BnPn(S)/Ag series (as presented in Figure 2b). Considering that a lower involvement in the (S(Se))− C1 bond should be compensated by a higher involvement in the (S(Se))− C1 bond stability but one that is reversed in phase compared to the Ag−S(Se) bond. This scenario is fully confirmed by the odd−even emission of the [M − S(Se)]+ fragment, which shows lower emission, i.e., higher stability of the (S(Se))− C1 bond, for odd-numbered members of the BnPn(S(Se))/Ag series. The fact that such an odd−even effect is not observed in the respective data obtained for the Au substrate indicates that the odd−even effect on film stability is less pronounced for the Au substrate than the Ag substrate.

To summarize the discussion above, the increase in the stability of the Ag(Au)−S(Se) bond caused by the change of the binding atom from S to Se or, to a much lower extent, by the odd−even change within the BnPn(S(Se)) series causes a reduction in the Se−C1 bond stability. The reduction in the Se−C1 bond stability results, in turn, in a shift of the valence electrons of the C1 atom toward the C2 atom, which leads to an increased strength of the C1−C2 bond, and so on. Following the previous DFT calculations, this effect should lead, in principle, to the oscillation in the relative stability of consecutive chemical bonds within the aliphatic chain for the S and Se SAMs on both Ag(111) and Au(111) substrates. The amplitude of these oscillations should decrease for consecutive bonds because the disturbances introduced into the electronic structure of the aliphatic chain by chemical bonding to the substrate via the headgroup atom become diminished at larger distances from the molecule−substrate interface: the disloca-
tion of the valence electrons becomes increasingly smaller. Such a prediction is confirmed by the data shown in Figure 5, which analyzes the emission ratio of fragments emitted from S- and Se-based SAMs as a result of the termination of four consecutive chemical bonds (see the schematic illustration in Figure 5a). Importantly, the effect of this oscillation for both Au(111) and Ag(111) substrates has the same phase, which is mutually consistent with the fact a higher bonding strength was observed for Se-based compounds for both types of substrates; therefore, if our explanation of this effect is correct, this defines the common phase of these oscillations. In addition, the amplitude of these oscillations for both types of substrates reduces as the number of consecutive chemical bonds increases, thereby supporting the proposed model.

There is, however, an alternative explanation of the oscillations presented in Figure 5 that we have to consider. In the current analysis of the data shown in Figure 5, we correlate the stability of consecutive chemical bonds in these SAMs with the emission efficiency of molecular fragments with (importantly) different lengths. One could, therefore, speculate that the observed oscillations in the relative intensity of this emission actually reflects an odd−even mechanism in the ionization efficiency that depends on the length of the emitted fragment, and thus the observed effect is not related to the stability of the respective chemical bonds, as proposed in the model above. To exclude such a hypothesis, further observation of this phenomenon was conducted by analyzing the [C$_{15}$H$_{15}$]+ molecular fragment emission from the series of BnPn(S)/Au(Ag) SAMs, i.e., without changing the mass of the analyzed fragment (Figure 6). As indicated in the previous section, a few crucial observations can be made at this point. First, the phase of the oscillations is independent of the type of the headgroup atom, which shows that both types of headgroup atoms give a binding energy of the S(Se)−C1 bond that is below the typical C$n$−C$n+1$ bond energy in long aliphatic chain; thus, this induces the same phase of oscillations in the binding energy of consecutive C−C bonds that propagate from the metal−molecule interface, where the disturbance occurs, into the middle of the molecular chain (see the schematic illustration in Figure 6d). Second, for both head groups, the amplitude of these oscillations vanishes quickly from the interface into the middle of the aliphatic chain, in accordance with the model proposed above. Third, the amplitude of these oscillations is significantly higher for the Se headgroup atom, in accordance with the lower stability of the Se−C1 bond compared to the S−C1 bond and thus, the higher stimulation for oscillations in the binding energy of consecutive chemical bonds for the Se headgroup atom. Fourth, the effect is very similar for both Ag and Au substrates, but a higher amplitude of the observed oscillations is noticed in the latter case, which indicates a higher binding energy of S and Se headgroup atoms with the Ag substrate compared to the Au substrate. For the S headgroup, this experimental observation is consistent with previous DFT calculations that predict a higher stability of the Ag−S bonding compared to the Au−S bonding for short alkanethiols on Au and Ag substrates. The common phase of oscillations shown in Figure 6a for the Au and the Ag substrates proves that the observed oscillation effect in the [C$_{15}$H$_{15}$]+ emission is not related to the odd−even structural effect in the BnPn(S)/Au(Ag) SAMs because in such a case, the phase of this effect would be reversed upon changing the substrate from Ag to Au.

To confirm that all the above analysis, conducted for the emission of the [C$_{15}$H$_{15}$]+ fragment, has a very general nature that is not dependent on a particular fragment, a fully analogical analysis has been subsequently performed for the emission of the [C$_{16}$H$_{17}$]+ and [C$_{17}$H$_{19}$]+ fragments, which are longer than the [C$_{15}$H$_{15}$]+ fragment by one and two CH$_2$ groups, respectively. Despite the reduction in the range of analyzed SAMs, due to the increased length of the analyzed fragments, all the observations above are the same. Thus, the analysis performed for all three types of fragments is internally consistent and fully confirms the model formulated above.

5. CONCLUSIONS

In conclusion, a systematic analysis of static SIMS (S-SIMS) data and selected exchange experiments performed for four homologous series of SAMs, which had a general form of BnPn(S)/Ag(Au) with n = 2−6, resulted in a few interesting observations concerning the subtle changes in the internal
energetics at the metal-molecule interface induced by the substitution of the headgroup atom (S → Se), and independently, the substrate (Ag → Au). These observations provide a new insight, which can be divided into three important categories.

The first and most relevant insight of the current paper is the purposeful design of SAMs. These results demonstrate that the modification of the headgroup atom from S to Se increases the strength of the chemical bonding with Au and Ag, which are the most commonly used metal substrates for the formation of SAMs. It is demonstrated that the Ag substrate enables a stronger binding with both S and Se head groups in SAMs compared to Au. In addition, the obtained data indicate the influence of the structural odd—even effect on the strength of the molecule–metal binding, which is apparently weaker than the impact of the S → Se or Au → Ag substitution. Finally, it is shown that an increased strength of the chemical bonding with the metal substrate has a strong impact on the stability of consecutive chemical bonds and, in particular, leads to a reduced strength of the bond between the headgroup and the rest of the molecule. In our opinion, this effect explains the lower thermal stability of selenium-based SAMs on gold compared to sulfur analogues, as reported in previous experiments. Despite the stronger bonding with the substrate for the Se-based SAMs, the thermal stability does not depend on the strongest bond but on the weakest bond in the adsorbed system; therefore, the reduced strength of the C–Se bond compared to the C–S bond may determine the lower thermal stability of Se-based SAMs. The alternative strength of the Au(Ag)–S(Se) and S(Se)–C bonds can also influence the conductivity of their respective SAMs. Specifically, a similar efficiency of charge transfer through the Au–S–C and Au–Se–C interface in SAMs was recently reported by us, which indicates that compensating the higher stability of the Au–Se bond by the lower stability of the Se–C bond results in an effectively similar redistribution of the electron density through the molecular framework and thus, a similar efficiency in charge transfer via the tunneling process. Because our current data show that substrate modification from Au → Ag and headgroup atom modification from S → Se qualitatively have very similar effects, we may expect a similar conductance for S- and Se-based SAMs on both Au(111) and Ag(111) substrates. Such a conclusion is supported by recent experiments that demonstrate a very similar conductance of alkanethiols on Au and Ag substrates.

The second insight provided by this paper is the application of S-SIMS. In our opinion, the results conducted for very broad and systematically modified groups of SAMs constitute a new and unique application of this method. Despite using high-energy projectiles, our results show oscillations in emission of different fragments, which are related to subtle changes in the stability of internal molecular bonds of the monolayer. Such information has not been obtained so far by any other technique. Two main advantages of S-SIMS, which seem to be crucial in this study, are the following: (i) the local nature of probing, i.e., the effectively analyzed mass spectra results from the impact of a single ion with no global change to the energetic state of the sample, as is the case with more traditionally used thermal or electrochemical desorption processes, and even more importantly, (ii) the extremely short probing time, i.e., the ion-induced desorption processes occur in the picosecond time scale, in contrast to thermal or electrochemical desorption where slow ramping of the global energies (temperature or potential energy, respectively) induces a structural evolution of the SAM/substrate system before the desorption process occurs and thus leads to a disconnected relationship between the original structure of the SAM and its stability.

The final category, and the most general one, is related to the observed oscillations in the stability of consecutive chemical bonds. This effect was identified for the first time in our recent paper, which indicated that its origin is very general in chemistry and is related to breaking of the translational symmetry in molecules. Experimentally, this fundamental conclusion was based on the similar odd—even efficiency in the emission of different molecular fragments from the BPhS(Se)/Au(111) series, as shown in Figure 6. For such an interpretation, however, it is necessary to prove that this effect is not related to the odd—even modification of the BPhS(Se)/Au(111) SAMs structure, but it instead reflects oscillations in the internal energetics of consecutive chemical bonds in the molecules, which become visible as the n parameter of the monolayer changes due to specific experimental conditions. The direct proof presented here shows that the nature of this odd—even effect on emission is completely independent of the Au → Ag substrate modification, which leads to a reversed phase of the structural odd—even effect. Moreover, by showing the correlation between the increased binding strength upon changing the substrate (Au → Ag) and the increased amplitude of these oscillations for both S- and Se-based SAMs, this paper fully confirms and expands on the earlier model proposed.

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