

Photoelectron spectroscopy study of irradiation damage and metal–sulfur bonds of thiol on silver and copper surfaces

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Abstract

Self-assembled 1-dodecanethiol monolayers (SAMs) on silver and copper surfaces have been characterized with X-ray photoelectron spectroscopy (XPS) using both the synchrotron radiation and conventional Mg K α excitation. Irradiation-induced changes in thiolate SAMs on Cu and Ag were observed. The identification of the sulfur species has been done. Results obtained confirm earlier studies of *n*-alkanethiols on silver. On copper (C₁₂S/Cu), the observed S 2p spectrum is quite broad but the use of different excitation energies enabled us to identify four sulfur species on the surface. A S 2p_{3/2} component of copper thiolate is observed at 162.6 eV. Three more doublets (161.9 eV, 163.2 eV and 163.8 eV) have been observed to develop during irradiation and they are assigned to chemisorbed sulfur on copper, to different dialkylsulfides and to sulfur–sulfur bonding.

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1. Introduction

Long-chain thiols form self-assembled monolayers (SAMs) upon adsorption on metal surfaces. These thin organic films are usually prepared by immersion of solid substrates in solutions containing reactants that spontaneously adsorb on the surface and form an ordered structure. The molecules are attached to the surface with a strong coordinative bond via the sulfur atom after the deprotonation of the –SH group of thiol molecule. The rest of the molecule is directed away from the metal surface due to the lateral interactions, forming structurally stable molecular films [1]. The most widely studied and best understood systems are

n-alkanethiolate SAMs on gold [1,2–5]. They are easy to prepare, chemically stable and have highly ordered structures. In this work, we have studied the adsorption of 1-dodecanethiol (C₁₂SH) on silver and copper. Although some studies of alkanethiol adsorption on Ag [1,6–10] and Cu [11–16] have been reported, the differences and similarities between the structures on substrate materials are not fully understood. SAMs can be used to control the interactions at the metal/ambient interface and are useful, e.g., in biological applications [17–19], for controlling the wetting properties [20,21], in lithographical applications [22], molecular electronics [23] and sensors [18,19]. Recently, special attention has been paid to the corrosion protection of copper surfaces with long-chain alkanethiol layers [11,12].

Thiol SAMs have been studied with many techniques [1,2–7] during the last decades. In this work, the adsorption of 1-dodecanethiol on silver and copper has been charac-

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terized using conventional as well as synchrotron-based X-ray photoelectron spectroscopy (XPS). XPS is an excellent method for studying the SAMs because it is sensitive to the chemical composition of the sample. However, the prolonged exposure to X-rays can cause degradation of the alkanethiol monolayers [4,5,24]. The most likely reasons for the degradation of organic adsorbates are sample heating, X-ray-induced and electron-induced damages. In the case of alkanethiolate monolayers, the most important factors are probably the photoelectrons and secondary electrons that are produced in the photoelectric processes [5]. Analysis of irradiation-induced damages is useful, since X-ray photoelectron spectroscopy is an often used method to consider thin organic films like the ones we have analyzed. X-ray-induced damage can be surface dependent, because the interaction of photon radiation with the substrate and the number of photoelectrons produced depends on the substrate material [25]. Although much is already known about the damage caused by low-energy electrons in SAMs, there is a lack of detailed knowledge of the processes that are unique to certain substrate monolayer combinations. Recently, studies about irradiation damages of alkanethiolate monolayers on Au [4,5,8,24], Ag [8], InP [5] and Pt [24] have been published. We show the effect of irradiation to the C₁₂S/Ag and C₁₂S/Cu systems and compare the former SAM with the latter one. To our knowledge, no studies concerning irradiation damage on alkanethiolate on copper have been considered so far. We present also a S 2p spectrum of pristine (not damaged) C₁₂S/Cu system. The spectra from pristine and damaged layers give information on the radiation-induced changes of the SAMs. The results can be used to interpret more complicated systems and to identify possible irradiation-induced damages on them.

In synchrotron-based photoelectron spectroscopy, quite low photon energies are available to invoke the photoelectric process. In this work, we have used excitation energies of 210–350 eV to study the S 2p region (about 160–165 eV), which produces photoelectrons with a kinetic energy of ca. 85 eV and results in very surface-sensitive spectra [26]. According to a universal curve [26], the value of inelastic mean free path λ is about two metallic surface layers for 85 eV kinetic energy. If the Al K α (1486.6 eV) or Mg K α (1253.6 eV) excitation is utilized, the surface sensitivity results in the inelastic mean free path of the electrons of much higher kinetic energy [27]. If the kinetic energy is 1000 eV, then λ is about eight atomic layers [26]. In this case, a large amount of the signal comes from the bulk metal, diminishing the information on the thin surface layer and necessitating long measurement times, especially for the S 2p spectra, which increases the possibility of irradiation-induced damage to the film. Also, the atom ionization cross-section [28] plays an important role for explaining the effect of photoelectrons of the substrate on SAMs especially, close to the Cooper minimum of the Cu 3p line. These cross-sections depend strongly on the photon energy.

2. Experimental

2.1. Sample preparation

The SAMs were prepared on polycrystalline silver (Goodfellow) and copper (Outokumpu, Finland) surfaces by spontaneous adsorption from solution. Prior to the adsorption, the surface (area ca. 0.5 cm²) was wet-polished with a SiC grinding paper (1000 mesh and 4000 mesh) and washed with pure water. Surfaces were then immersed in a 1 mM solution of 1-dodecanethiol CH₃(CH₂)₁₁SH (denoted later as C₁₂SH) or hexanethiol CH₃(CH₂)₅SH (C₆SH) in deoxygenated ethanol for approximately 24 h. After the treatment, every sample was carefully rinsed with ethanol and water to remove the weakly adsorbed species from the surface. Sample treatment was consciously kept as simple as possible. The C₁₂S/Cu and C₆S/Cu samples were always measured immediately after the sample preparation but there was a delay of three days between the preparation and the synchrotron-based measurements of the C₁₂S/Ag samples. During this time, the samples were kept in a sealed container and protected from exposure to light and dust.

2.2. Analysis

The conventional XPS measurements were carried out with a Perkin-Elmer PHI 5400 spectrometer in our laboratory and the high-resolution core-level photoelectron spectroscopy studies were done at MAX-lab (National Electron Accelerator Laboratory for Synchrotron Radiation Research, Nuclear Physics and Accelerator Physics) in Lund, Sweden. Beamline I411 at MAX II was used [29]. The measurements were done at room temperature in a vacuum better than 2×10^{-9} Torr with an energy resolution of about 40 meV. The binding energy scale was calibrated by setting the Ag 3d_{5/2} or Cu 3p_{3/2} peaks of bulk metals to values 368.26 eV or 75.14 eV, respectively [30]. The calibration of the standard XPS measurements was carried out for Ag substrate also with 3d_{5/2} but for the Cu substrate, Cu 2p_{3/2} emission line of bulk metal (932.66 eV) was used [30]. The XPS Cu 3p or Ag 3d, C 1s, S 2p spectra and in some cases also O 1s lines were detected in order to study the interaction between C₁₂SH and metal. The peak shapes of the core level photoelectron spectra were analyzed with a Unifit program [31]. A Shirley-type background correction and a Voigt peak shape were utilized. The S 2p_{3/2} and S 2p_{1/2} lines were fitted with a fixed binding energy difference of 1.18 eV and an intensity ratio of 2:1, reflecting the multiplicity of the S 2p_{3/2} and S 2p_{1/2} energy levels. The reproducibility of the data was confirmed by measuring the data from different positions or from different samples.

3. Results and discussion

For the analysis of the SAM, we concentrate on the C 1s and S 2p photoemission spectra. The bulk metals have

Table 1
XPS binding energies obtained in this study and assignment of them

Emission line	Binding energy (eV)	Assignment	Comments	
Ag 3d _{5/2}	368.26	Bulk metal	Used for calibration	
Cu 3p _{3/2}	75.14	Bulk metal	Used for calibration	
Cu 2p _{3/2}	932.66	Bulk metal	Used for calibration	
C 1s	285.10 ± 0.05	(CH ₂) _n	Irradiation-induced degradation of the chains shifts the peak towards smaller BE	
S 2p _{3/2}	160.90 ± 0.05	S–Ag	Chemisorbed sulfur	
	161.85 ± 0.05	–C–S–Ag		
	161.9 ± 0.1	S–Cu	Chemisorbed sulfur	
	162.60 ± 0.05	–C–S–Cu		
	163.2 ± 0.2	Irradiation-induced sulfur species		Most probably: –C–S–C–
	163.8 ± 0.2	Irradiation-induced sulfur species		Some possibilities: –C–S–S–C–, S–S and S ⁰
	165.6	SO		

been used for the calibration of the energy scale. A summary of the observed binding energies and their assignments are presented in Table 1.

3.1. Conventional XPS

The standard XPS measurements were done in order to study the changes of the spectrum shape as a function of irradiation time. The same spectrum has been recorded many times from the same spot of a specimen. Relative intensities of all elements present on the pristine surfaces are presented in Table 2. These values do not match with the real atomic concentrations of the samples due to the fact that the considered elements have different depth profiles in the samples, so that the emission signals are differently attenuated. In the pristine SAMs, the measured C 1s emission lines are symmetric and they all can be fitted with one peak having a Gaussian–Lorentzian shape (BE: 285.13 eV and FWHM 1.39 eV for C₁₂S/Ag, and BE: 285.16 eV and FWHM 1.41 eV for C₁₂S/Cu). The symmetry of the initial C 1s emission peak of pristine SAMs indicates that the molecules have formed a standing-up phase on the surface. If there were a lying-down phase, which is supposed to exist at the beginning of the adsorption process [32], the peak would be broadened [6] and could not be fitted with only one component. During the XPS measurement, the C 1s emission line shifts to smaller BEs and at the same time, its FWHM increases indicating changes and disordering in the aliphatic chains. The same phenomenon can be observed for thiol layers on both substrates being demonstrated in Fig. 1. The effect of the radiation on the layer structure can also be seen in the change of atomic concentrations on the surface as a function of the measurement time. For instance, the total amount of carbon

Table 2
Relative intensities in percentages of all elements present on the pristine surfaces

Sample	Metal (%)	Carbon (%)	Sulfur (%)	Oxygen (%)
C ₁₂ S/Ag	36.82	60.05	3.14	0.00
C ₁₂ S/Cu	18.11	70.50	3.18	8.21

decreases significantly. This is a clear evidence of the breaking of the hydrocarbon chains and of the loss of carbon from the surface.

Figs. 2 and 3 show the S 2p emission spectra as a function of irradiation time for C₁₂S/Ag and C₁₂S/Cu, respectively. The evolution of a new structure in the S 2p spectra of C₁₂S/Ag is clearly evident in Fig. 2. The differences of the spectrum can be related to the radiation-induced changes of the chemical bonding of sulfur atoms. A similar behavior has been reported earlier for alkanethiol layers on gold [4,5,8,24] and silver [8] substrates. The origin of the new structure on the higher BE side of thiolate has been attributed to a disulfide species [5] or the incorporation of sulfur into the alkyl matrix via its reaction with an irradiation-induced

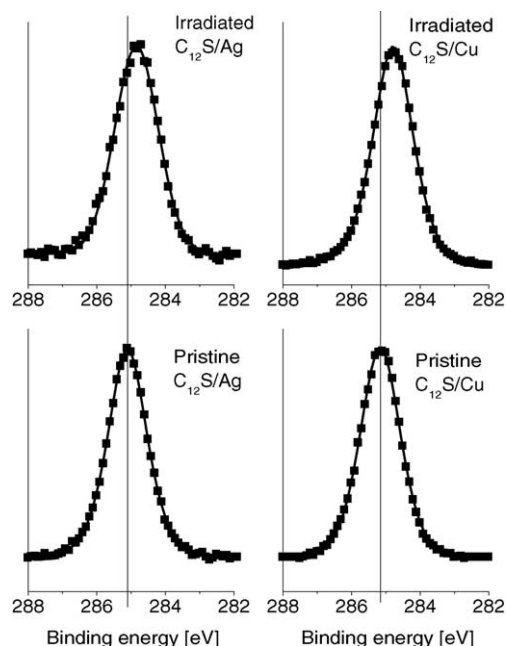


Fig. 1. The C 1s XPS spectra for pristine and irradiated C₁₂S/Ag and C₁₂S/Cu. The positions of C 1s peak maximum of pristine layers are marked by thin solid lines to guide the eye. The spectra are normalized to the same intensity.

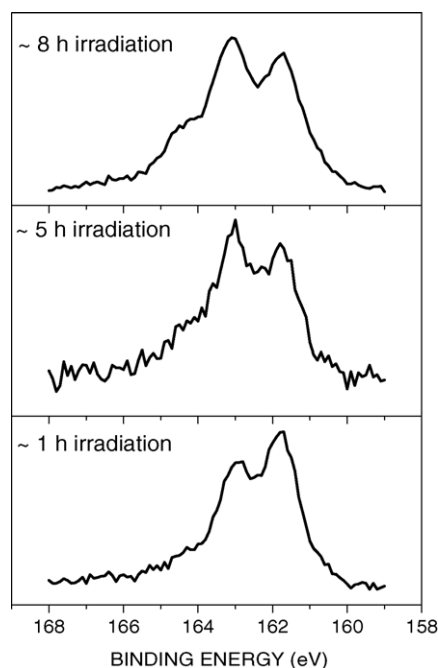


Fig. 2. The S 2p XPS spectra measured from $C_{12}S/Ag$ as a function of irradiation time using Mg $K\alpha$.

carbon radical [4]. All the measured S 2p spectra of $C_{12}S/Ag$ can be fitted with a combination of three doublets having S $2p_{3/2}$ binding energies of about 160.9, 161.85 and 163.2 eV. The doublet with a binding energy of about 161.85 eV is attributed to surface thiolate and does not depend on irradiation time. The origin of these doublets is discussed in the context of high-resolution core-level spectroscopy measurements.

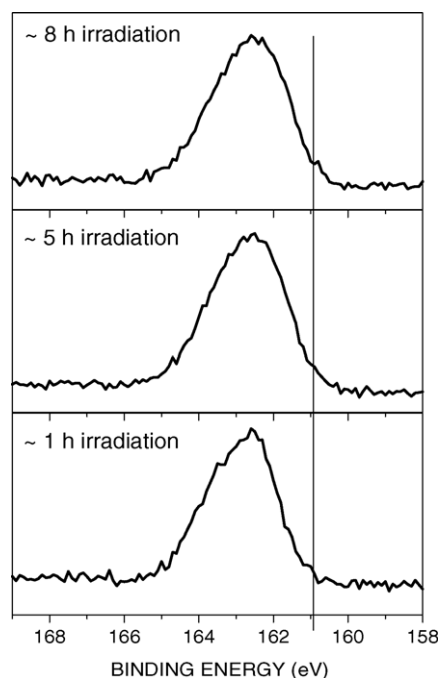


Fig. 3. The S 2p XPS spectra measured from $C_{12}S/Cu$ as a function of irradiation time. The vertical line is a guide to demonstrate the shift.

Table 3

Intensity vs. Mg $K\alpha$ X-ray exposure results for $C_{12}S/Ag$ SAM concerning the amount of sulfur on the surface

Time (min) ^a	163.8 eV	163.2 eV	161.85 eV	160.9 eV	Total amount of sulfur
0–44	–	–	100	–	100
44–293	–	15	45	5	65
293–382	3	20	34	5	62
382–455	4	17	24	5	52

The sulfur species are referred by the S $2p_{3/2}$ binding energy values of the fitted spectra. The atomic concentration values are normalized so that the amount of sulfur is 100% at the beginning.

^a Time 'zero' is the starting point of the measurement.

In contrast to $C_{12}S/Ag$, there is no obvious variation in the shape of the S 2p spectrum of thiolate on copper (Fig. 3) with the Mg $K\alpha$ excitation. The resolution of the conventional XPS is not sufficient to distinguish between different sulfur species and the fitting procedure for these broad spectra is therefore somewhat uncertain. However, a small shift towards smaller binding energies can be observed. The S–Cu bond is strong and the dissociative desorption of alkyl chains upon C–S bond breaking is characteristic for alkanethiolate films on copper surfaces [13,14]. The S $2p_{3/2}$ signal that can be attributed to chemisorbed sulfur appears at ca. 161.9 eV (161.5 eV according to reference [14]) on copper. The small shift of the sulfur peak towards smaller BEs as a function of irradiation time reveals its existence.

A comparison of presented two groups of spectra indicates that there is a deviation in the response of thiolate layer to radiation. The differences in the formation of irradiation-induced sulfur species on $C_{12}S/Ag$ and on $C_{12}S/Cu$ can be related to the thiolate–substrate bond, as it has been suggested for both the $C_{18}S/Au$ and $C_{18}S/Ag$ interfaces as well as the $C_{12}S/Au$ and $C_{12}S/Pt$ ones [8,24]. Differences can also depend on the radiation/substrate interactions. The fitting of the spectra has been done in order to study in more detail what species appeared as a result of X-ray exposure and what were the rates. The S $2p_{3/2}$ binding energies of used doublets are listed in Table 1. Intensity versus the X-ray exposure results in both studied systems ($C_{12}S/Ag$ and $C_{12}S/Cu$) concerning the amount of sulfur on the surface are presented in Tables 3 and 4. The true X-ray intensity on the sample surface could not be determined because of the differences in tube positioning and, consequently, exposure times have been used instead of irradiation doses. The distribution of sulfur to the

Table 4

Intensity vs. Mg $K\alpha$ X-ray exposure results for $C_{12}S/Cu$ SAM concerning the amount of sulfur on the surface

Time (min) ^a	163.8 eV	163.2 eV	162.6 eV	161.9 eV	Total amount of sulfur
0–50	–	9	79	12	100
50–213	–	10	47	21	78
213–303	–	11	23	33	67
303–516	–	13	20	28	61

Different sulfur species are referred as in Table 2.

^a Time 'zero' is the starting point of the measurement.

different species is presented. The values are normalized so that the amount of sulfur is 100 in the beginning. The real sulfur/metal ratios are 0.085 and 0.18 for S/Ag and S/Cu, respectively, obtained from the survey spectra measurements lasting less than 1 h from the beginning of the first sweep.

The data presented in Tables 3 and 4 show clearly the decrease in the total amount of sulfur as a function of irradiation time. During about 8 h of irradiation, the S/Ag ratio drops from a value of 0.085 down to 0.044 and the S/Cu ratio decreases from 0.18 to 0.11 which means that roughly 50% of sulfur has disappeared from both surfaces. Data presented for the C₁₂S/Ag system (Table 3) point out how the –C–S–C– peak (163.2 eV) grows from 0 to a value of 20% and then it starts to decrease again. For C₁₂S/Cu system, 9% of total sulfur is –C–S–C– type already at the beginning of the XPS measurement when the irradiation time is less than 1 h. Sulfur–metal bond scission is much more probable when a copper substrate material is used instead of silver. The intensity of dialkylsulfide component increases slowly during the extended measurements and in contrast with the C₁₂S/Ag system, the intensity of the S–Cu component increases drastically. This result and an increase of the amount of atomic sulfur on the surface as a function of measurement time support the earlier mentioned S–C bond scission. Sulfur that has been bound to carbon atoms of earlier aliphatic chains now falls away from the surface together with carbon. According to the atomic concentration values obtained from measured survey spectra, about 50% of the layer can be destroyed with Mg K α radiation-induced photoelectrons. After this damage, the situation stabilizes.

3.2. High resolution core level spectroscopy (HRXPS)

The intensity and the energy of a Mg K α radiation are quite large. This radiation penetrates rather deep below the surface film and produces a large number of photoelectrons, which cause film degradation. The core level measurements (HRXPS) have been performed for the thiol samples in order to increase the resolution and the surface sensitivity of the spectra. The effect of surface sensitivity is compensated

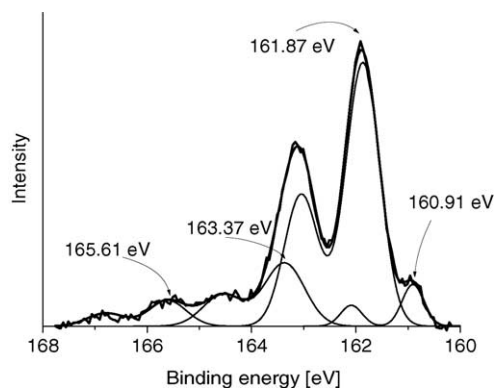


Fig. 4. Fitted high-resolution core-level photoemission (HRXPS) spectrum of S 2p emission line measured from C₁₂S/Ag.

with the energy dependence of the photoionization cross-section of substrate atoms. This phenomenon affects the number of escaping photoelectrons which are damaging the surface monolayer. Typically, 250 eV beam energy was used and with the corresponding wavelength, the total ionization probability of core levels is much larger than for an energy of 1250 eV which is used for conventional XPS measurements [28]. However, a short measurement time can lower the risk of SAM degradation. Synchrotron-based measurements were performed for Ag 3d, Cu 3p, O 1s, C 1s, S 2p and valence band energy regions. The shape of C 1s emission line was used as an indicator of layer quality. All studied layers were of good quality. A special attention was paid to the S 2p region and the high-resolution emission lines are presented in Figs. 4–6. Narrow peak widths obtained with HRXPS are necessary for the accurate fitting of the S 2p spectrum lines of studied systems.

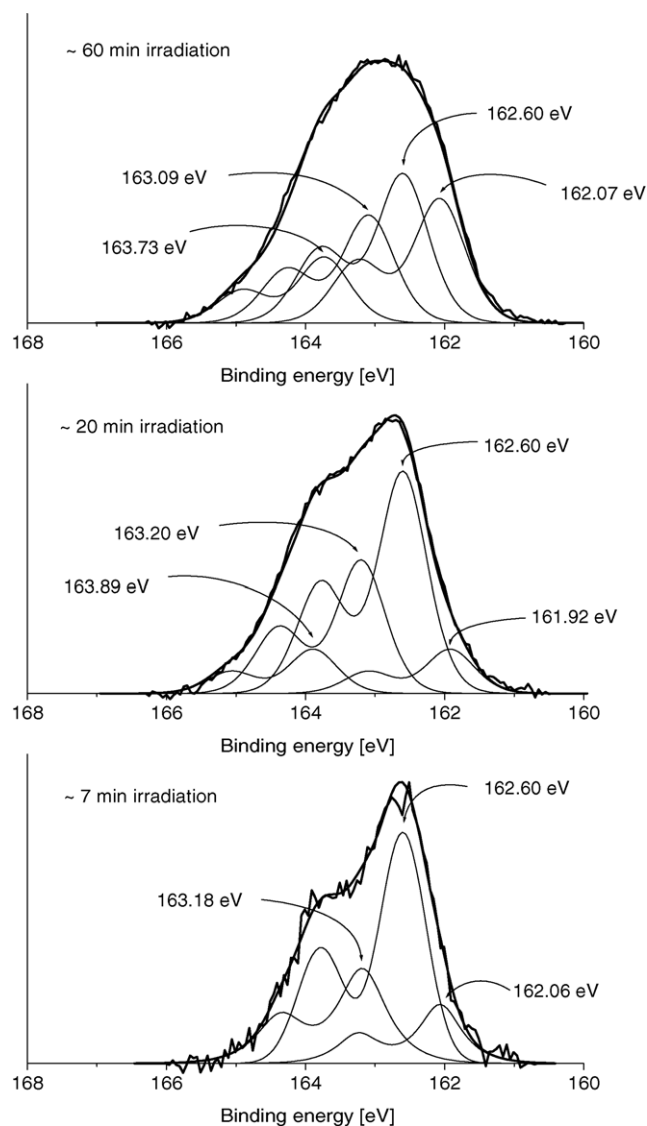


Fig. 5. High-resolution (HRXPS) spectrum of S 2p emission line measured from C₁₂S/Cu.

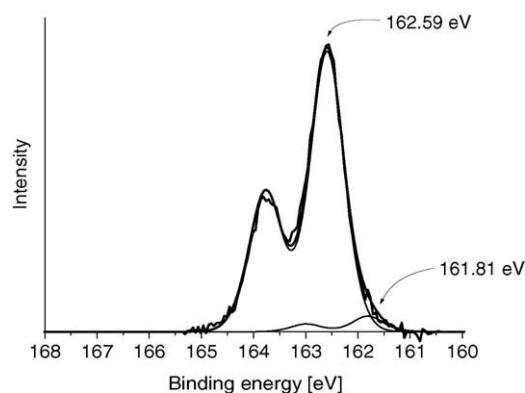


Fig. 6. High-resolution (HRXPS) spectrum of S 2p emission line measured from C₆S/Cu.

In the C₁₂S/Ag system, the observed binding energies of sulfur 2p_{3/2} (160.91, 161.87, 163.37 and 165.61 eV; Fig. 4) correlate well with those of Wang et al. [9], Zharnikov and Grunze [1] and Heister et al. [10]. The lowest binding energy peak (160.91 eV) is in a region characteristic of metal sulfides and it can be assigned to chemisorbed sulfur. The S 2p_{3/2} BE of Ag₂S is about 161 eV. Previously obtained values, 160.7 eV [33] and 161.3 eV [34,35], have been presented earlier. The S 2p_{3/2} BE 161.87 eV can be attributed to surface thiolate. The binding energy of atomic-like sulfur that is bonded to metal is lower than the binding energy of thiolate on metal. The formal oxidation state of sulfur decreases when the carbon chain breaks away from the surface. Typically, a shift of the S 2p binding energy is about 1 eV [36,37]. It has been observed to be due to conversion of thiolate to atomic sulfur. The relative intensity of the doublet with the S 2p_{3/2} BE at 163.37 eV increases significantly and it can be seen in the XPS spectra of Fig. 1, too. This component is typically referred to as ‘irradiation-induced’ in many studies concerning the thiol SAMs on Au and Ag substrates [5,8,24]. It has been identified as a disulfide [5] and to a dialkylsulfide [4,9] formed by incorporation of the sulfur atom in the carbon chains. Recently, an exposure of alkanethiol SAMs to atmospheric oxygen has been shown to induce considerably rapid sulfur oxidation on palladium [38]. We attribute the small component at high BE in Fig. 4 similarly for air oxidation. This small oxygen-related peak (S 2p_{3/2} BE: 165.61 eV) appears on the spectrum due to the fact that there was a delay between the preparation and the measurements of the C₁₂S/Ag sample. The component of a binding energy of 165.61 eV does not appear for other reported systems, because those were always measured immediately after the sample preparation.

In this work, four doublets were used to fit the high-resolution S 2p spectra of the irradiated C₁₂S/Cu system (Fig. 5). After an extended measurement time, the shape of the spectrum becomes so distorted that no individual peaks can be identified in the raw spectrum, which hampers the accurate determination of the BEs. However, a good fit can be obtained using four doublets with the S 2p_{3/2} BEs at ca.

161.9, 162.6, 163.2 and 163.8 eV. These BE values can be used to fit all the measured high resolution and conventional XPS spectra. The whole series of measurements (done with different excitation energies and irradiation times) were fitted with components having the same binding energies and the similar FWHMs. Only the relative intensities of the species are allowed to vary. The bottom spectrum of Fig. 5 required ca. 7 min irradiation time and shows relatively little radiation-induced changes. The intensity of the synchrotron radiation is high (a rough estimate of the photon flux on the sample is 10¹¹–10¹³ ph/s) and in 20 min, the spectrum has changed so much that the clear doublet-like shape begins to fade. After 1 h, the shape of the spectrum is similar to that of the conventional XPS spectra in Fig. 3. This is a consequence of modifications in the chemical environment of sulfur atoms. The film degradation starts as soon as the beam meets the film.

Fitting of broad spectra presented in Fig. 5 is risky. Nevertheless, we do it. We were able to successfully fit more than 20 S 2p HRXPS spectra of long-chain thiol on copper with the mentioned four doublets (supplementary files).

The S 2p_{3/2} signal at about the BE of 161.9 eV is connected with chemisorbed sulfur (S–Cu). As it was mentioned earlier, the S–Cu bond is strong and the C–S bond breaking is characteristic for alkanethiolate films on copper surfaces [13,14]. Our detection of the formation of S–Cu is in accordance with the results of Vollmer et al. [13] who have reported the coexistence of thiolate and sulfide species on the saturated alkanethiolate monolayers on Cu (1 0 0) at room temperature as well as at higher temperatures. They give a S 2p_{3/2} BE of 161.3 eV for atomic sulfur adsorbed on copper. Also, the S 2p binding energies of different copper sulfides are quite near to our observed value. The S 2p_{3/2} BEs of CuS and Cu₂S have been reported to be 161.6 eV [39] and 161.7 eV [40], respectively.

The S 2p_{3/2} binding energy 162.6 eV can be attributed to thiolate C₁₂S/Cu (literature value for R–S–Cu compounds ca. 162.6 eV [13–16]). The BE of this component was checked with measurements of the C₆SH sample and the doublet is presented in Fig. 6. The signal was obtained immediately after positioning the 250 eV photon beam onto the sample surface. The measurement time was only 1 min. In this case, the spectrum is practically free from irradiation-induced effects and a clear doublet can be seen at a BE of 162.59 eV (S 2p_{3/2}). The FWHM of both components is 0.79 eV. Only one small additional doublet is needed on a BE of 161.81 eV. This BE value matches quite well with an assumed BE of 161.9 eV for chemisorbed sulfur S–Cu.

In previous studies, the irradiation-induced sulfur species in alkanethiol SAMs on gold and other substrates have often been assigned to disulfide moiety [5]. However, an alternative interpretation has been recently proposed, namely an incorporation of sulfur as dialkylsulfide into the alkyl matrix via bonding to irradiation-induced carbon radicals in the adjacent aliphatic chains [4]. The sulfur species on Cu and Ag with BE at ca. 163.2 eV, observed in this work, can also be

assigned as a dialkylsulfide. The binding energy agrees well with those previously reported (163.14 eV [4], 163.3 eV [24] and 163.4 eV [9]).

In Fig. 5, a new doublet appears at more than 7 min irradiated layers and is probably induced by X-ray-induced photoelectrons from the ionized substrate atoms and by secondary electrons breaking the bonds within the SAM. This doublet cannot be fitted to the S 2p spectra of standard XPS measurements of C₁₂S/Cu because of the quite broad FWHMs caused by the unmonochromatized Mg K α radiation. The binding energy of ca. 163.8 eV corresponds well with that of elemental sulfur (S⁰; literature value 164.2 eV [41], 163.9 eV [42] and 163.7 eV [43]). Observation of S⁰ with UHV techniques is not trivial, because of the high vapor pressure of elemental sulfur. However, it can be observed even at room temperature, when it is formed on the surface during analysis. The component with a BE of 163.8 eV can also be assigned to unbound disulfides based on the corresponding BE values reported by Siegbahn and co-workers [41]. In addition, the Raman spectra of irradiated thiolate films reveal typical fingerprints of disulfides [5]. The existence of sulfur dimers (disulfides) may be a consequence of surface oxide because copper oxidizes rapidly during the sample preparation. It has been proposed that adsorbed dodecanethiol molecules are oxidized to disulfides at the edges of the CuO islands [11]. However, the reaction consumes all the CuO layer [15] and the monolayer is formed on the reduced surface. In our work, the O 1s spectrum region in the BE range of 525–540 eV showed no sign of oxygen indicating that there is no detectable amount of Cu₂O left on the surface. Also, no peak at 163.8 eV was observed in high-resolution core-level measurements of pristine (not irradiated) samples. This component appears only after a long irradiation, which suggests that the possible disulfides on copper form as a result of generated photoelectrons.

No sulfinate or sulfonate species are detected on any of the surfaces. Also, there were no peaks at higher binding energies (167–169 eV). This indicates that no oxygen-containing sulfur species are present on the surface in either case.

4. Conclusions

Standard XPS and high-resolution core-level photoelectron spectroscopy (HRXPS) have been used to characterize adsorption of 1-dodecanethiol on silver and copper surfaces. The irradiation damage in monolayers was studied as a function of time as well as with different excitation energies. The decrease in the total amount of sulfur was observed. We utilized the chemically shifted S 2p core-level photoelectrons as a probe to investigate the formation of X-ray irradiation-induced sulfur species on surface thiolate. In the C₁₂S/Ag SAMs, the observed sulfur species were identified as chemisorbed sulfur, surface thiolate, irradiation-induced dialkylsulfide and oxidized sulfur (BEs: 160.91, 161.87, 163.37 and 165.61 eV, respectively). The corresponding species in the C₁₂S/Cu SAMs exhibited the S 2p_{3/2} bind-

ing energy at 161.9 eV (chemisorbed sulfur), 162.6 eV (surface thiolate) and 163.2 eV (dialkylsulfide). In addition, the component with BE of 163.8 eV was observed for both studied systems after a long irradiation time. It may be assigned to unbound disulfide but also with elemental sulfur. The identification of irradiation-induced species is essential in order to correctly interpret XPS spectra of SAMs.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.elspec.2004.10.001](https://doi.org/10.1016/j.elspec.2004.10.001).

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