



Influence of initial oxygen on the formation of thiol layers

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Abstract

In this study, X-ray photoelectron spectroscopy (XPS) has been used to study thin organic films. For comparison, monolayers were formed on clean and air-exposed metal substrates. Obtained results show that thiols remove contamination oxygen from gold, silver, platinum and copper surfaces. The tightly packed thiolate layers can be formed. In addition, oxygen does not take part in the final bonding of molecules to the surfaces.

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1. Introduction

Self-assembled monolayers (SAMs) are spontaneously formed, well-ordered films on surfaces. They are used to control the interactions at the metal/ambient interface. Many studies have presented useful applications of them. One possible use of self-assembled monolayers is to protect metal against corrosion. The barrier properties of SAMs largely result in the length and organization of the alkyl chains. Thick barriers of thiols can block electron transfer and hinder the transport of water, oxygen, and aggressive ions to the metal surface, extending the

protection against corrosion markedly. Therefore, alkanethiol covered metal systems result in novel materials with an unusual corrosion resistance. Investigations of surfaces covered by long-chain alkanethiols reveal that a good protection can be obtained [1–4]. Self-assembled monolayers are also used in controlling wetting properties [5]. By changing from terminal $-\text{CH}_3$ to $-\text{OH}$ groups, one alters the wetting properties from hydrophobic to hydrophilic. Organosulfur derivatives coordinate strongly to many sulfide and metal surfaces and form monomolecular films. The widespread use of thiols, for example xanthates in ore flotation, provides an important application of using the surface hydrophobicity to control industrial processes [6]. SAMs can be utilized in biological applications to serve as a

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new tool to provide model biocompatible surfaces [7]. Nowadays, there is a booming demand for miniaturized biosensors for diagnostic applications. Long-chain alkane thiols produce a highly packed and ordered surface, which can provide a membrane-like microenvironment, useful for immobilizing biological molecules. The high selectivity of biological molecules together with other characteristics of them offers a great promise to exploit immobilized biological molecules as efficient and accurate biosensors [8,9]. Self-assembled monolayers are also important in applications for nanotechnology [10–12]. One criterion for the development of nanoelectronic devices is being able to position and pattern molecular components selectively on surfaces. Soft lithography with SAMs enables alternative ways for creating small two- and three-dimensional chemical patterns on material surfaces [13]. With SAMs electronic components the size of few nanometers can be constructed.

Some of the most commonly used molecules forming self-assembled monolayers are alkyls bearing mercapto group (thiols). Sulfur compounds have a strong affinity to transition metal surfaces. In the liquid phase method of forming SAMs, the molecules are dissolved in an organic solvent and they are let spontaneously adsorb to the substrate material. The –SH group of thiol molecule suffers deprotonation at the surface and molecule binds to the surface through the S atom. The forming mechanism of thiol SAMs on Au, Pt, Ag and Cu substrates is proposed to be basically similar. In self-assembled monolayers, the packing and ordering are determined by the contributions of both chemisorption and intra- and interchain non-bonded (e.g., van der Waals, steric, repulsive, electrostatic) interactions. The interplay between interchain forces and interactions with the surface, combined with entropic effects, determines both the conformation of the individual chains within the assembly and their packing as well as ordering with respect to each other [14]. More details about the growth and the structure of self-assembled monolayers are presented in Ref. [15]. The orientation of the individual molecules, structure and thereby characteristics of the ultrathin self-assembled monolayer are dependent on the substrate material: its structure and cleanliness. Anyway, as this study will show, the initial oxygen contamina-

tion (originating from air) on the surface does not necessarily prevent formation of the tightly packed thiolate layer.

We have used X-ray photoelectron spectroscopy (XPS) method to study thiol layers. Peaks related to substrate metal, oxygen, carbon and sulfur were observed in the XPS spectra. Provided only mechanical polishing combined with rinsing is used to clean up substrate metals, then traces of oxygen are detected by XPS on the thiol-treated samples with an estimated content of typically 1–2 at.% and for copper substrate even 10 at.%. This indicates some contamination within the monolayers and/or oxidation of the metal substrate. The contamination of the initially pure metal samples is normally caused by a short time exposure to the air before immersion in the thiol solution and again before inserting the sample to the spectrometer vacuum. The chemical composition of air includes several oxygen containing species: O₂, H₂O, CO₂, O₃, OH radical and other components [16,17]. The aim of this work is to perform special studies about the influence of surface oxygen on the formation of SAMs. The first part of this study concerns the influence of thiol treatment on the initially adsorbed air contamination, the second part is dealing with the influence of contamination on the formation of a thiol layer. The third part describes the situation that oxygen has no effect on the shape of the XPS spectra of S 2p emission. This means that it does not take part in the final bonding of molecules to the surfaces.

2. Experimental

2.1. Sample preparation

The SAMs were prepared on polycrystalline gold, platinum, silver (all from Goodfellow) and copper (Outokumpu Copper, Finland) surfaces by a spontaneous adsorption from the solution. Prior to the adsorption, the surface (area ca. 0.5 cm²) was wet-polished with a SiC grinding paper (1000 and 4000 mesh) and washed with pure water. After polishing, the sample was introduced in to the ultra high vacuum (UHV) chamber and it was cleaned by repetitive Ar⁺ bombardment and heating in UHV until the XPS indicated a clean surface. Then the sample was moved

to the treatment solution. Provided that no initial oxygen was desired to the surface, the sample was moved to the solution in a nitrogen-containing carrier chamber. In the case when the atmospheric oxygen was needed to gather to the sample, the surface was kept 1 h in air (laboratory environment) before inserting it to the treatment solution. During that time the samples were contaminated for example by hydrocarbons and oxygen containing species from the ambient. Dodecanethiol, $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$ (marked C_{12}SH later on the text), was used for chemical treatment of the specimen. Thiol was used as purchased from Aldrich (99%). Surfaces were immersed in a 1 mM solution of thiol in deoxygenated ethanol for approximately 24 h. After that treatment every sample was carefully rinsed with ethanol and water to remove the weakly adsorbed species from the surface.

2.2. Film characterization

The XPS spectra were measured with the Perkin-Elmer PHI 5400 spectrometer. All the XPS data were acquired using analyzer pass energy of 35.75 eV for narrow scan spectra and 89.45 eV for wide scan survey spectra (0–1100 eV). The electron take-off angle was 45° . Monochromated Al $\text{K}\alpha$ excitation was used. The power of the X-ray source was 300 W. The measurements were done at room temperature and the base pressure in the analyzer chamber was ca. 2×10^{-9} Torr during the spectrum detection. The spot diameter of the characterized area is about 2 mm. The binding energy (BE) scale of the spectrometer was calibrated using the standard Au $4f_{7/2}$ (BE = 83.98 eV) reference line. The binding energy of the most intense line from the metal substrate (namely Au $4f_{7/2}$: 83.98 eV; Pt $4f_{7/2}$: 71.20 eV; Ag $3d_{5/2}$: 368.26 eV or Cu $2p_{3/2}$: 932.67 eV [18,19]) was normally utilized as an internal standard to correct the possible binding energy shift. The peak shapes of the spectra were analyzed with a Unifit program [20]. The linear or Shirley background correction and the Voigt peak shape were used for C 1s, S 2p and O 1s emission lines. The asymmetric peak shapes were used for metal lines. The S $2p_{3/2}$ and S $2p_{1/2}$ doublets were fitted with a fixed binding energy difference of 1.18 eV and an intensity ratio of 2:1, which reflects the multiplicity of the S $2p_{3/2}$ and S $2p_{1/2}$ energy levels.

3. Results and discussion

3.1. Influence of thiol treatment on the amount of initially adsorbed oxygen

The chemical compositions of the surfaces before and after thiol treatment were compared using XPS. Before the first series of measurements the substrates have been in air for 1 h after sample cleaning. After that time XPS survey spectra were measured from air-contaminated surfaces and atomic concentrations of the detected elements were determined. The samples were then put into the thiol solution for 24 h. The second series of measurements were done after the formation of a thiolate layer. In the XPS survey spectra, the line-intensities originating from thiol molecule (carbon and sulfur lines) increase in size and the line-intensities of the pre-adsorbed species (oxygen lines) decrease noticeably. The survey spectra that have been measured from the same silver sample before and after the thiol treatment is presented in Fig. 1 as an evidence for oxygen decrease. The spectra clearly show the disappearance of the O 1s line having a binding energy of about 531 eV.

Table 1 presents the atomic concentrations of all the air-contaminated samples before and after the thiol solution treatment. Due to the difficulties, which arise from calculating the inelastic mean free path (IMFP) for the photoemitted electrons in the organic layer, the precise atomic concentrations cannot be given. The oxygen/metal ratio has been calculated to eliminate the effect of attenuation caused by the hydrocarbon chains of C_{12}SH . The changes in oxygen/metal ratio presented in table indicate clearly that oxygen has been removed from all the studied surfaces after an immersion of the sample into the thiol solution. The ratio O/Au diminishes from the value 0.45 to the value 0.06, O/Pt from 0.47 to 0.24, O/Ag from 0.25 to 0.02 and O/Cu from 0.84 to 0.50. The presented experimental results of changes in atomic concentrations correlate well with those previously obtained by other methods for other self-assembling systems [21]. From Au and Ag surfaces adsorbed oxygen is completely removed and replaced by thiol. Also, on Pt surfaces the change in the amount of oxygen is remarkable. The residual oxygen on Pt could be bound to carbon of thiol molecules. On the copper surface, where an oxide layer can be supposed to be formed on the

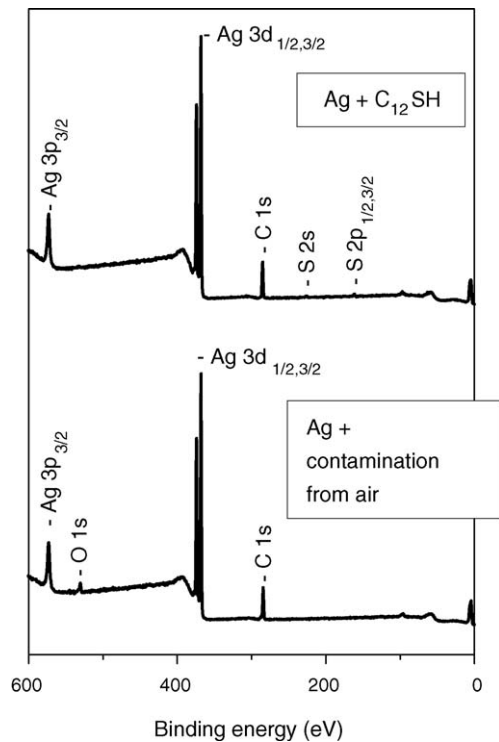


Fig. 1. The survey spectra that has been measured from the same silver sample before and after the thiol treatment.

surface during the air exposure, some oxygen is still present after thiol treatment but the amount is diminished on this case, too. The detailed analysis of O 1s and Cu 2p spectrum regions (Fig. 2) reveal the

Table 1

The atomic concentrations of the intentionally air-contaminated samples measured before and after thiol solution treatment

	Au	C	S	O	O/Au
Before thiol solution	34.26	50.35	0	15.4	0.45
After thiol solution	37.92	58.66	1.27	2.14	0.06
	Pt	C	S	O	O/Pt
Before thiol solution	36.19	43.25	0	16.98	0.47
After thiol solution	35.32	55.49	0.75	8.44	0.24
	Ag	C	S	O	O/Ag
Before thiol solution	35.21	55.87	0	8.92	0.25
After thiol solution	37.87	59.24	2.3	0.59	0.02
	Cu	C	S	O	O/Cu
Before thiol solution	29.62	45.56	0	24.82	0.84
After thiol solution	16.11	71.91	3.98	7.99	0.50

The amount of oxygen is large at the beginning, because after cleaning the samples they were kept in air for 1 h in order to gather atmospheric oxygen. Also, the amount of carbon impurities is high at the beginning.

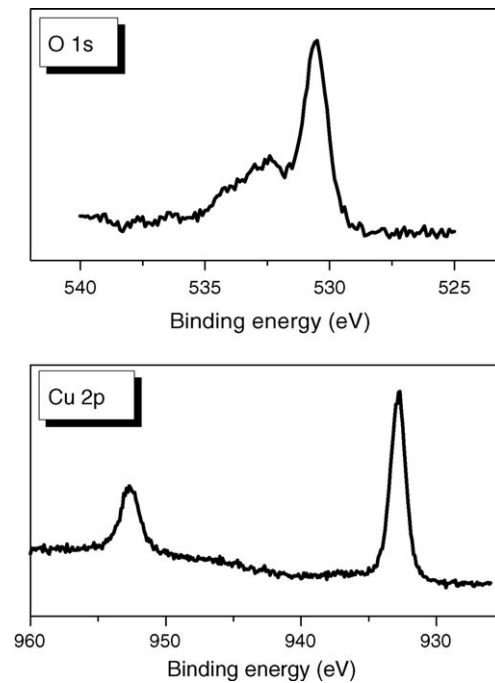


Fig. 2. The O 1s (upper) and Cu 2p_{1/2,3/2} (lower) spectra that have been measured from an air-treated copper sample after the formation of a thiolate layer.

presence of copper oxide on the surface. A peak at about 530.3 eV can be assigned to Cu₂O [19]. The Cu 2p spectrum shows no shake-up structure and it is reasonable to expect that there is no divalent copper (species like CuO or Cu(OH)₂) on the surface. Also a broad line in a binding energy of about 531–535 eV can be observed in the O 1s region. This kind of a spectrum is typical for an air-contaminated surface having physisorbed oxygen-containing species on the surface. The effect of copper oxide on the monolayer formation is controversial. In some earlier studies, an embedding of oxide under the SAM has been proposed [22], but in others it is denied [23].

3.2. Influence of the initially adsorbed oxygen on the formation of thiol layer

We have made comparative studies concerning the adsorption of thiol on the clean samples and initially air-treated samples to see how the surface contamination affects the formation of thiolate layer on a metal surface. Atomic concentrations are presented in

Table 2

The atomic concentrations of the studied samples measured after thiol solution treatment from the surfaces with and without initial air-contamination

	Au	C	S	O	S/Au
Initial oxygen on the surface	37.92	58.66	1.27	2.14	0.033
No initial oxygen on the surface	38.79	59.30	1.91	0	0.049
	Pt	C	S	O	S/Pt
Initial oxygen on the surface	35.32	55.49	0.75	8.44	0.02
No initial oxygen on the surface	39.39	55.95	4.66	0	0.12
	Ag	C	S	O	S/Ag
Initial oxygen on the surface	37.87	59.24	2.3	0.59	0.061
No initial oxygen on the surface	37.53	58.19	3.38	0.91	0.090
	Cu	C	S	O	S/Cu
Initial oxygen on the surface	16.11	71.91	3.98	7.99	0.25
No initial oxygen on the surface	16.68	75.00	4.21	4.11	0.25

Table 2. The presence of small amounts of oxygen on the initially clean surfaces could be due to the adsorption of contaminants during the sample transfer from the solution to the spectrometer vacuum even if the transfer took only few minutes of time. It is also possible that some oxygen containing species have been adsorbed on the sample surface during the solution treatment. Actually, an adsorption of ethanol is possible, but in the measured TOF-SIMS spectra (not presented in this study) the amount of C_2H_5 leaving the sample is for all the substrates ($C_{12}SH$ -treated Au, Pt, Ag, Cu) about same or slightly less than that of C_3H_7 . This indicates that adsorption of ethanol has not appeared. Anyway, the amount of oxygen on the clean surfaces is negligible compared to the oxygen concentration on air-treated surfaces. Our results show that in the case of Au, Ag and Pt substrate materials the initial oxygen reduces the adsorption of thiol on the surface. On contrary to the before mentioned substrate materials copper oxide seems to increase thiol adsorption. A catalytic effect of surface oxygen on the film formation of docosanethiol from solution to polycrystalline silver is proposed in some earlier

studies [21]. That does not seem to be the case according to our results with silver substrate, but it seems possible with the copper one.

3.3. Influence of initially adsorbed oxygen on the chemical shifts in the XPS spectra measured from monolayers grown on air-contaminated and clean metal surfaces

In this section, chemical shifts in XPS spectra measured from monolayers grown on air-contaminated and clean metal surfaces in 1 mM dodecanethiol in ethanol are reported and discussed.

The existence of initial oxygen on the metal surface before the thiol treatment has no influence on the shape of Au 4f, Pt 4f, Ag 3d or Cu 2p spectra if they are measured after an adsorption of thiol. Similar spectrum shapes have been obtained from initially clean and initially air-contaminated surfaces. Fitted spectra have typical energy positions and shapes of bulk metal lines (Au 4f_{7/2} emission line: BE = 84.0 eV and FWHM = 0.9 eV; Pt 4f_{7/2} emission line: BE = 71.2 eV and FWHM = 1.0 eV; Ag 3d_{5/2} emission line: BE = 368.3 eV and FWHM = 0.9 eV; Cu 2p_{3/2} emission line: BE = 932.7 eV and FWHM = 1.20 eV). The copper surface is proposed to have some oxide left after the thiol treatment. There is no shake-up satellite structure in the spectra, which means that there is no divalent copper, but the quite broad FWHM of Cu 2p_{3/2} emission line suggests that there may be a monovalent copper in addition to the metallic one.

The obtained bulk metal peaks have been used for calibration. For a molecule adsorbing on a surface one can sometimes find core-level shifts for the substrate atoms, which bond directly to the molecule because charge transfer has occurred between the bonding substrate and adsorbate atoms, and the formal oxidation state of an atom can be detected as a chemical shift in its XPS spectra. Unfortunately, core-level binding energy shifts do not necessarily follow, although the atoms are in different environments. The adsorption of thiol can also reconstruct the metal surface. During monolayer assembly the surface of substrate metal relaxes and mobile atoms are detected on the surface [24]. The real surface has always defects. There are different adsorption sites on a surface. This can cause binding energy shifts to the XPS spectra. Anyway, the limited energy resolution of

the XPS equipment as well as the fact that the most emitted photoelectrons are from the bulk and not from the surface region preventing the observation of adsorption induced shifts in observed metal core-level peaks.

For all the spectra a broad line is observed on the O 1s binding energy region 531–535 eV. This kind of spectrum is typical for an air-contaminated surface, where one can find several different physisorbed oxygen-containing species. Metal oxide, adsorbed hydroxide groups, oxygen, water and carbonate ions are the most probable contaminants. The intensity of this line is low, as it can be assumed based on the atomic concentrations presented in Table 1. Both copper samples (initially air-contaminated and initially clean) have a narrow peak at 530.3 eV, which can be assigned to Cu_2O or CuOH .

Initial oxygen has no influence on the shape of C 1s spectra of thiol-treated sample if the substrate material is Au, Ag or Cu. In the case of the Au substrate a narrow symmetric peak at 284.9 eV (FWHM = 1.3 eV) can be assigned to hydrocarbon chain of ‘standing’ thiol molecules of the self-assembled monolayer. The small peak (intensity ratio to the main peak is about 1:25) at about 286 eV can be connected to C–S or C–O bonds. The peak associated with the hydrocarbon chain of ‘standing’ thiol molecules is observed at 285.3 eV (FWHM = 1.3 eV) on the Ag substrate. On the Cu substrate a hydrocarbon chain related peak is observed at the BE 285.3 eV (FWHM = 1.3 eV). On contrary to the Au, Ag and Cu substrate materials initial oxygen influences on the shape of C 1s spectra measured from the $\text{C}_{12}\text{SH}/\text{Pt}$ substrate. The emission lines obtained from monolayers grown on air-contaminated and clean platinum surfaces in 1 mM dodecanethiol in ethanol are presented in Fig. 2. The peak at about 284.9 eV can be associated with a hydrocarbon chain of standing thiol molecules of the self-assembled monolayer. The line at about 286.2 eV can be ascribed to C–O. The peak at 284.3 eV could indicate laying hydrocarbon chains [25]. Sum-curve of individual components matches with the measured peak, though it cannot be distinguished from the figures. The shape of the spectrum is in agreement with the atomic concentration values presented in Table 2. The small S/Pt ratio is an indication of a bad quality of a thiolate layer. Fig. 3 together with Table 2 shows that the shape of a

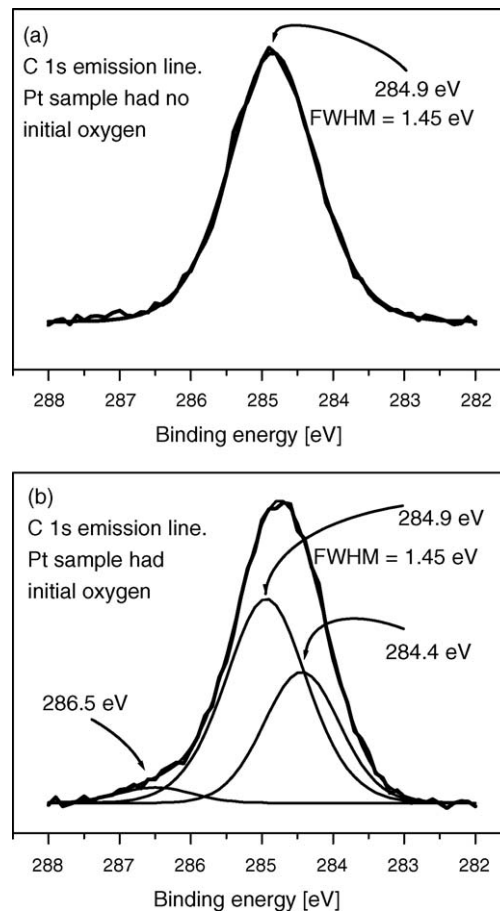


Fig. 3. The C 1s emission lines from C_{12}SH -treated: (a) initially clean and (b) initially air-contaminated surfaces.

C 1s emission line is a good indicator of the quality of the layer.

The C 1s emission line has to be carefully interpreted. It shifts towards smaller binding energies as a function of XPS-measurement time. This property is due to the irradiation induced chemical changes in the hydrocarbon chains [26]. Even the initial energy position of the C 1s emission line for an alkanethiol monolayer deviates noticeably depending on the substrate material. The difference of the C 1s binding energy can be explained by the final state effects due to the alkyl matrix which has a different packing density and orientation of the molecular chains on different substrates [26]. If the C 1s signal does not show any sign of an influence of contamination, one has to expect that the remaining oxygen is buried under the

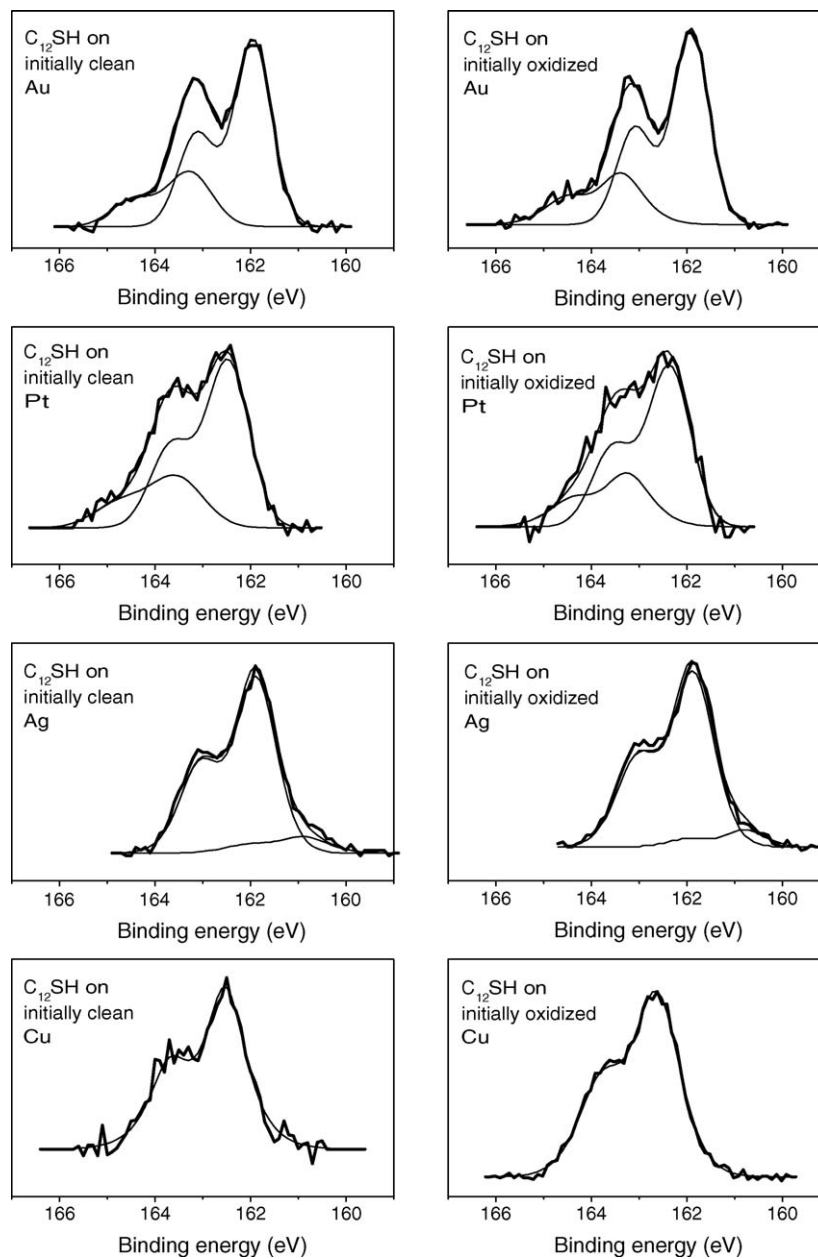


Fig. 4. The S 2p spectra measured from monolayers grown on clean and air-contaminated metal surfaces.

thiol layer and should be seen in the S 2p spectra, too. The existence of islands is also possible.

No oxidized sulfur species (S 2p BE > 166 eV) [27] such as sulfate or sulfide were detected by XPS on any of the samples. The S 2p spectra measured from

monolayers grown on clean and air-contaminated metal surfaces are presented in Fig. 4. The binding energies of the sulfur photoemission are consistent with those of a thiolate monolayer. Oxygen has no influence on the shape of S 2p spectrum measured

from the initially air-contaminated and initially clean gold surface after adsorption of thiol. The S 2p_{3/2} BE 161.9 eV (FWHM = 0.9 eV) can be connected to the RS–Au bond [28] and the smaller peak (intensity ratio to the main peak is roughly 1:3) at about 163.3 eV (FWHM = 1.1 eV) can be assigned to the radiation induced species [28]. Also, the S 2p spectra measured from the Ag substrate remain unaffected even if there is pre-adsorbed oxygen on the surface before immersing the sample to the ethanolic solution of thiol. The spectrum region can be fitted with two doublets. The main doublet has a binding energy of 161.9 eV for S 2p_{3/2} (FWHM = 1.0 eV) and a smaller doublet (intensity ratio to the main peak is about 1:10) is at a BE of 160.9 eV (FWHM = 1.1 eV). The feature having a binding energy of 161.9 eV can be associated with the RS–Ag bond [29] and the smaller peak at 160.9 eV can be attributed to atomic sulfur on Ag [30]. The measurement times have been kept so short that no irradiation induced sulfur species can be observed on the Ag surface. When the substrate material is platinum, again initial oxygen has no influence on the shape of the S 2p spectra. Two doublets have been used for the fitting. The main component is at the BE = 162.5 eV (FWHM = 1.0 eV) and another doublet (the intensity ratio to the main peak is about 1:3) has BE = 163.3 eV (FWHM = 1.3 eV). The binding energy 162.5 eV can be ascribed to the RS–Pt [31] bond and the smaller peak at 163.3 eV can be assigned to R–S–R [31]. The spectrum of the initially oxidized copper sample can be fitted with one doublet having a S 2p_{3/2} BE of 162.6 eV (FWHM = 1.2 eV). For the fitting of S 2p measured from thiolate on initially clean copper surface one doublet is needed having a S 2p_{3/2} BE of 162.6 eV (FWHM = 1.0 eV).

4. Conclusions

It is obvious from the above discussion that the adsorption of thiol removes oxygen from the surface. Regardless of the used substrate material the oxygen concentration is reduced after a thiol treatment, but in the case of Au, Ag and especially with the Pt substrate initial oxygen reduces the amount of thiol on the surface. On contrary to the before mentioned substrate materials a high oxygen precoverage seems to increase

thiol adsorption in case of the copper substrate. The sulfur 2p XPS binding energies are not affected by initial oxygen, indicating that sulfur does not have a contact with the air-contaminated surface but rather with the clean metal.

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