

J. Synchrotron Rad. (1999), 6, 793–795

Self-assembled monolayers of 4-aminothiophenol on copper surfaces studied by grazing-incidence X-ray absorption spectroscopy

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Self-Assembled Monolayers (SAMs) of 4-Aminothiophenol on copper surfaces have been investigated, using Grazing Incidence X-Ray Absorption Spectroscopy (GIXAS). The surface sensitivity of this technique allows us to characterize the chemisorption process by XANES and EXAFS measurements in fluorescence mode at the sulfur- and copper-K-edge. Our results are consistent with 4-Aminothiophenol (4-ATP) bound to the surface through the sulfur headgroup. From EXAFS analysis two different interatomic distances between sulfur and next neighbour copper atoms $d_{S-Cu_1} = 2.26 \text{ \AA}$ and $d_{S-Cu_2} = 3.1 \text{ \AA}$ could be determined. Data indicates occupation of deep three-fold hollow positions of sulfur with significant reconstruction of first layer copper atoms on preferably textured (111)-surfaces. Adsorption of 4-ATP as disulfide, described in a "sulfur-pairing model", is not supported by absorption data in the XANES region. EXAFS analysis on the other hand gives some evidence for the presence of a sulfur dimer moiety, with a sulfur-sulfur spacing of $d_{S-S} = 2.1 \text{ \AA}$. Depending on the preparation procedure, oxidation of thiol-molecules occurs, leading to a coexistence of sulfate-ions and intact 4-ATP on metal surfaces due to partial cleavage of the S-C bond.

Keywords: self-assembled monolayers (SAMs), grazing incidence X-ray absorption spectroscopy, EXAFS.

1. Introduction

In 1983, R.G. Nuzzo and D.L. Allara proved the formation of stable, ordered and densely-packed monolayer films of alkanethiols ($HS(CH_2)_nX$, $X = CH_3, CH_2OH, COOH...$) on gold surfaces. Modification of the substrate is realised by the strong affinity of the thiol-headgroup to gold. The organosulfur species formed from the chemisorption of the thiol-molecule is a gold(I)-thiolate (Nuzzo, 1983). On copper and silver surfaces high-quality films can be prepared as well. Variation of the chain-terminating functional group X of the thiol-molecules offers the possibility to control surface properties in a wide range.

In X-ray deep etch lithography metal surfaces were modified with 4-Aminothiophenol (4-ATP, $H_2NC_6H_4SH$) to enhance the adhesion of polymer-resists, e.g. polymethylmetacrylate (PMMA), on metal substrates. 4-ATP was found to be an effective adhesion promoter on gold. However, modification of copper substrates did not lead to a significant improvement (Schmidt, 1996).

In this paper first results of the application of Grazing Incidence X-Ray Absorption Spectroscopy (GIXAS) on 4-ATP-modified metal surfaces are reported. EXAFS and XANES measurements in fluorescence mode were carried out to characterize the bonding mechanism of 4-ATP on copper surfaces. Additionally, the influence of oxidation effects of metal surfaces on the functionality of modified surfaces is a point of major interest in this paper.

2. Experimental

Freshly evaporated metal films on Si(111)-wafers were immersed in a 1 mMol 4-ATP/ethanol solution for 24 h. After removing physisorbed layers of 4-ATP by washing in pure ethanol, samples were transferred to the experiment and investigated immediately. Measurements were carried out at the storage ring ELSA, Bonn university, running at 2.3 GeV with an average current of 35 mA (Althoff, 1978). The grazing incidence experiment is located at beamline BN2. Synchrotron radiation is monochromatized by a double-crystal monochromator of Lemonnier-type using InSb (111) or Ge (422) crystals with an energy resolution of about 1 eV (Chauvistré, 1987). The synchrotron beam is collimated vertically to $150 \mu\text{m}$ by a slit-system before hitting the sample at an angle of incidence below the critical angle of total external reflection. The critical angle was determined by measuring the specular reflectivity of the incoming X-ray beam as a function of incidence angle as shown in fig. 1. Since the critical angle θ_{cr} depends linearly on the photon wavelength (Born, 1978), we selected a photon energy of $E = 9000 \text{ eV}$ for reflectivity measurements, which is above the Cu-K-edge, to determine a lower limit for θ_{cr} . The half-maximum value of the reflectivity curve leads to an estimated critical angle $\theta_{cr} = 0.4^\circ$.

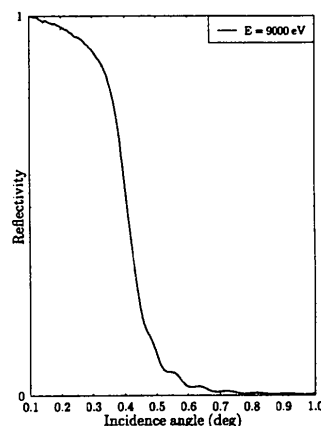


Figure 1

Reflectivity of a copper surface: Determination of the critical angle of external total reflexion θ_{cr}

Typically an angle of incidence of $\theta = 0.2^\circ$ was chosen in our investigations to ensure the surface sensitivity. This results in a penetration depth of the X-ray beam of 5nm on copper surfaces at the Cu-K-edge, as depicted in fig. 2. Increasing the angle of incidence up to a value close to the critical angle leads to increase of penetration depth and so to loss of surface sensitivity. Since the penetration depth is nearly independent of the energy of the radiation for incidence angles below the critical angle, we can assume a constant information depth for all measurements at the Cu-K and S-K-edge. Spectra were obtained by measuring the induced fluorescence intensity above the sample using an EG&G Si-Li semiconductor detector (energy resolution $\Delta E = 200 \text{ eV}$). Data acquisition time was 3 h for EXAFS-spectra of moderate quality (8 s per step, step width for EXAFS $\Delta E = 0.75 \text{ eV}$, for XANES $\Delta E = 0.3 \text{ eV}$). Reference spectra of 4-Aminothiophenol, copper and copper sulfate were measured in transmission mode. As an energy standard at the S-K-edge we used $ZnSO_4$, with its whiteline at $E = 2481.7 \text{ eV}$. For data reduction and analysis the EXAFS program package of Ertl/Bertagnolli (including FEFF 6) was used (Ertl, 1991). The energy position E_o of the absorption edge was determined using the

derivative-method. EXAFS functions were derived using a spline fit for approximation of the atomic absorption coefficient μ_o . The k -range in the analysis was limited to $3 \text{ \AA}^{-1} < k < 10 \text{ \AA}^{-1}$.

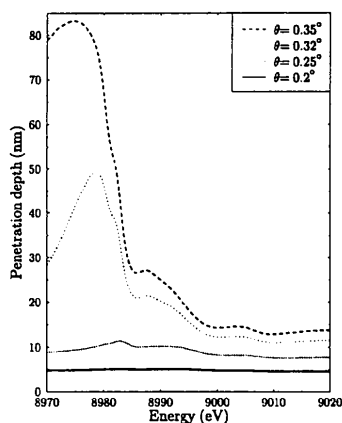


Figure 2

Calculated penetration depth of radiation on a copper surface: below the critical angle the penetration depth has a small constant value of about 50 \AA

3. Results and Discussion

Fig. 3 shows S-K-XANES spectra of 4-ATP and of a self-assembled monolayer of 4-ATP on a copper surface. In the reference spectrum two resonances (features a,b) at energies $E_1 = 2471.3 \text{ eV}$ and $E_2 = 2473.2 \text{ eV}$ are visible. These absorption features can be attributed to the conjugated π -electron-system of the aromatic 4-ATP molecule, leading to double and single bond character of the sulfur-carbon bond (Smith, 1994). Feature a corresponds to $1s \rightarrow \pi^*$ and feature b to $1s \rightarrow \sigma^*$ transitions. Sulfur is in the oxidation state +II. There are hardly any significant differences between the spectra of the reference and the SAM in the XANES region. Cleavage of the S-H bond and formation of a copper(I)-thiolate species on the surface, as predicted in the literature (Nuzzo, 1983), seems not to influence the π -character of the sulfur-carbon bond. The same result was found in the case of a gold surface. In contrast, absorption spectra of SAM on silver surfaces clearly reflect incorporation of $p\pi^*$ -orbitals in the silver-sulfur interaction, leading to the absence of the low-energy resonance in the XANES region (Schlieben, 1998). These differences give evidence for different bonding schemes of the self-assembling process on various metal substrates. Indeed, as discussed by Ulman (1996), alkanethiols are bound differently to Au(111) and Ag(111) surfaces due to the effects of lateral discrimination of chemisorption potentials and electrostatic charge-charge repulsion. The Au(111) surface is energetically more heterogeneous indicated by an energy difference of 6 kcal mol^{-1} between on-top and hollow adsorption sites of thiolate molecules (on Ag(111) the energy difference is $3.3 \text{ kcal mol}^{-1}$). Adsorption on on-top sites may therefore compete more with that on hollow-sites for Ag(111) surfaces leading to a higher net charge on sulfur atoms, e.g. $-0.7e$ for on-top sites compared to $-0.4e$ for hollow sites. Charge-Charge repulsion among both S and Au atoms on the other hand is a second effect distinguishing between the different bonding schemes. In conclusion, sulfur headgroups of SAMs on Au(111) are believed to occupy hollow sites resulting in a commensurate $\sqrt{3} \times \sqrt{3}R30^\circ$ overlayer, while on Ag(111) a $\sqrt{7} \times \sqrt{7}R10.9^\circ$ structure is assumed with every

seventh metal atom in an on-top position (Ulman, 1996).

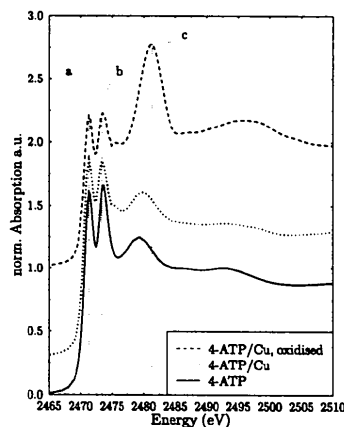


Figure 3

S-K XANES spectra of 4-ATP-SAM on a copper surface: features a,b and c refer to oxidation states +II and +VI respectively

Our data agrees with the assumption of a larger amount of charge transfer from metal substrate atoms to the sulfur headgroup in the case of a silver surface compared to gold and copper surfaces suppressing $1s \rightarrow \pi^*$ transitions. This gives evidence for sulfur occupying hollow and on-top sites on Ag(111). Additionally, EXAFS analysis (see below) leads to a S-Cu next neighbour bond distance of $d_{S-Cu} = 2.26 \text{ \AA}$, which is a typical value for hollow site bonding (Fernandez, 1995), while the corresponding S-Ag distance is much larger: $d_{S-Ag} = 2.44 \text{ \AA}$ (Schlieben, 1998). Adsorption of 4-ATP as a disulfide in a "sulfur-pairing model" proposed by Fenter (1998) is not supported by our XANES data. The presence of a dimer S-S moiety should be detected by a corresponding resonance in the XANES region. This modification is not present in the absorption spectra.

In fig. 3 an additional spectrum is shown from a 4-ATP/Cu sample, which was exposed to air and light for several hours before investigating. The occurrence of a new resonance at $E = 2481 \text{ eV}$ in the absorption spectrum is evident (feature c). This new feature has to be attributed to an oxidized sulfur-species on the surface in the oxidation state +VI (Chauvistré, 1987). As discussed by Rieley (1995) during investigations on the photooxidation of alkylthiol monolayers self-assembled on gold surfaces, exposure of SAMs to air and light results in the oxidation of the monolayer leading to sulfonate-species bound to the surface through oxygen. In contrast to this conclusion, we believe our data indicate a partial conversion of copper(I)-thiolate to coppersulfate due to cleavage of the S-C bond in the 4-ATP molecule, in agreement with Lewis (1995). Intact 4-ATP and CuSO_4 coexist on the surface, resulting in a reduced functionality, due to desorption of cleaved carbon-rings and formation of SO_4^{2-} ions in the presence of oxygen. This surface oxidation is responsible for the lack of adhesion promoting effects of 4-ATP modified copper substrates, as described by Schmidt (1996). The presence of coppersulfate on the surface was verified by measurements at the Cu-K-edge. In fig. 4 absorption spectra of oxidized and non-oxidized SAM on Cu are compared with CuSO_4 and Cu as references at the Cu-K-edge. Characteristic resonances at 8979 eV for Cu (feature d) and at 8993 eV for CuSO_4 (feature e) are emphasized. The spectrum of the non-oxidized SAM looks much zerovalent copper-like due to a penetration depth of the radiation of around 50 \AA , which is a much larger value than the assumed

monolayer thickness of 7 Å for a perpendicular geometry of 4-ATP molecules with respect to the surface (Kim, 1992). In the case of the oxidized sample the spectrum contains a superposition of zerovalent copper and copper in the oxidation state +II. The similarity to the spectrum of the CuSO₄ reference supports strongly the assumption of the oxidized surface species being CuSO₄.

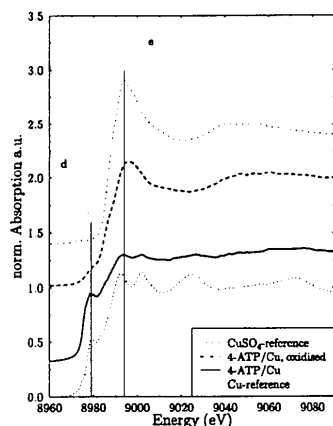


Figure 4
Cu-K XANES spectra of oxidized and non-oxidized SAM compared with Cu and CuSO₄ references

In order to determine the bonding geometry of thiol-molecules on the Cu surface, EXAFS investigations at the S-K-edge were performed. In fig. 5 the EXAFS-function of the SAM on copper is depicted for a k -range between $3 \text{ \AA}^{-1} < k < 10 \text{ \AA}^{-1}$.

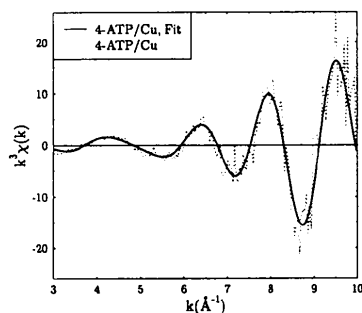


Figure 5
EXAFS-function at the S-K edge of 4-ATP-SAM on copper for a k -range $3 \text{ \AA}^{-1} < k < 10 \text{ \AA}^{-1}$

Fourier transformation to R-space gives interatomic distances between sulfur and neighbour atoms in different coordination shells, shown in fig. 6. Analysis of the EXAFS-data with a 3 shell fit, including the next neighbour carbon atom and copper atoms of the first and second substrate-layer leads to bond distances $d_{S-Cu_1} = 2.26 \text{ \AA}$ and $d_{S-Cu_2} = 3.1 \text{ \AA}$ for first layer and second layer copper atoms respectively and a S-C interatomic distance of $d_{S-C} = 1.86 \text{ \AA}$. Assuming a dominantly crystalline (111)-surface structure with a copper-copper nearest neighbour spacing in the (111)-plane of $d_{Cu-Cu} = 2.56 \text{ \AA}$, we can conclude that the S atoms occupy deep three-fold hollow sites. Reconstruction of the top Cu layer occurs. Following the argumentation of Imanishi et. al. (1998) we found a lateral displacement of Cu atoms of 0.8 \AA and a polar angle of the S-Cu bond with respect to the surface normal of $\omega = 63^\circ$. The calculated S-C bond length is larger than the corresponding value of the 4-ATP molecule ($d_{S-C} = 1.80 \text{ \AA}$), which is a result of

charge transfer from copper surface atoms to the sulfur headgroup reducing the π -character of the S-C bond.

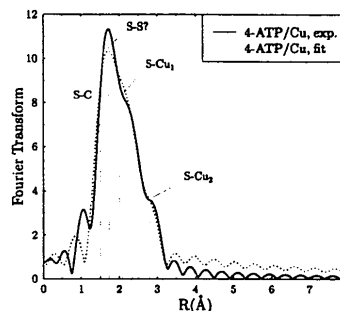


Figure 6
Fourier-transform of EXAFS function: the contributions of different backscatterer-shells are emphasized

The best results in the fitting procedure could be achieved assuming an additional sulfur backscatterer, as predicted by Fenter (1998). We could determine a S-S spacing of $d_{S-S} = 2.1 \text{ \AA}$, which is close to the predicted value of 2.2 \AA . The derived S-Cu distance of $d_{S-Cu_1} = 2.26 \text{ \AA}$ is similar to values estimated for the sulfur headgroup at the on-top site of a Au(111) surface in this model. Even the larger S-Cu distance of 3.1 \AA seen in the Fourier-transform is explained by the "sulfur-pairing model" as a non-bonding distance between the second sulfur atom and the surface (Fenter, 1998). This gives evidence of sulfur adsorption as a dimer with one sulfur atom bound to the surface at an on-top position and the other sulfur atom located vertically higher above the surface. However, as stated above, there is no verification of this model by the XANES spectra at the S-K-edge.

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