Chemical Reactions of Alkanethiolate Monolayers on Au and Ag Substrates with Free Radical-dominant Plasma: Alkyl Chains and S/Metal Interface

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Abstract
This work utilizes synchrotron light source to study self-assembled monolayers (SAMs) using thiols (H$_2$S-(CH$_2$)$_n$(CH$_3$)$_2$) as sulfur anchor group from solution onto Au (111) or Ag (111) surface. On the alkanethiolate (AT) SAMs surface, low-density N$_2$ downstream microwave plasma creates the activated alkyl chains, meanwhile, plasma species affect diversely to S/Au and S/Ag interfaces. Such plasma-induced process is performed in a reduced pressure and the modified AT SAMs surface is characterized in ultra-high vacuum using sample-transferring system. Experimental result using X-ray photoelectron spectroscopy has demonstrated that the alkyl chains are reactive with plasma species and neighboring oxygen, the C-O, C-N and C=O bonds can be found. The N, O-containing structures mostly result from chemical reactivity of free radicals in plasma. Sulfur anchor onto Ag (111) surface is much resistant to the reactive plasma species, compared with that onto Au (111) substrate, the alkyl chains on Ag (111) substrate are removed successively. The consequences may result in high binding strength of the S/Ag interface, and dimensional factors such as tilt angle and shielding domain of the alkylthiols upon metal. The latter is correlated with reactive characteristic of free radicals-dominant plasma primarily to the exposure of the AT SAMs and subsequent events of structural disorder.

Keywords: alkanethiolate SAMs surface, N$_2$ plasma, free radicals, chemical reactivity, tilt angle

Introduction

Self-assembled monolayers (SAMs) have attracted considerable interest from both the scientific and practical viewpoints. Considering the practical aspect, these films, in which the headgroup of an adsorbate covalently bonds to a solid substrate, while the chainlike molecular tail sticks out from the substrate, provide a means to tailor surface properties, such as wetting, lubrication, adhesion, and corrosion. These properties can be controlled by both the selection of suitable molecules and the physical modification of the respective SAMs through their exposure to ions, X-ray photons, UV light or electrons.

In this study we applied nitrogen downstream microwave plasma to SAMs of alkanethiols (AT) on polycrystalline (111) Au and Ag substrates. The SAMs were placed into plasma afterglow region separated by an extensive flowing pathway from the zone, where plasma excitation by the microwave field was performed. We expected that this positioning will enable to expose the SAMs predominantly to free radicals and minimize the effects producing by other plasma constituents, especially by electrons and ions. Due to numerous collisions of these species with the walls of the pathway quartz tube during their transfer to afterglow region, they lose kinetic energy and become incapable to re-excite neutrals or affect a SAM to an essential extent. However, it was very likely that adsorbrates on the walls of the pathway quartz tube, typically oxygen-containing substances, will be partially removed by plasma flow, recombined with nitrogen plasma as oxygen-containing nitrogen plasma, and projected to the surface of SAMs. Note that oxygen in different excited forms is chemically much more reactive, compared with similar states of nitrogen.
In the following, we will give a brief description of the experimental procedure and setup with a special emphasis on the design of the plasma source and on the plasma characterization.

Materials and methods

Formation of SAMs

The substrates were prepared by evaporation of 100-300 nm of gold or silver on titanium-primed (5 nm) polished single crystal Si(100) wafers (Silicon Sense). These films predominantly exhibit an (111) orientation as, e.g., concluded from the distinctive forward-scattering maxima in the angular distributions of the Au 4f and Ag 3d photoelectrons and from the characteristic binding energy (BE) shift of the Au 4f surface component. The SAMs were formed by immersion of the substrates in an ethanolic 1mM solution of octadecanethiol [C18: CH₃(CH₂)₁₇-SH] (Fluka Chemicals) for 24 hrs. After the immersion the samples were carefully rinsed and cleaned with ethanol, and blown with dry and pure nitrogen. The contact angle of the C18 SAMs (measured by sessile drop method) was found to be ~108°, as could be expected for the hydrophobic CH₃ surface.

Plasma density measurement

The afterglow plasma in the vicinity of the sample, inside the preparation chamber, was characterized using the Langmuir probe (Figure 2) connected to an electrometer (Keithley, model 6514). This invasive, electrostatic probe utilizes 10 mm long tungsten wire of 0.25 mm in diameter as the probing tool. Using the I-V curves provided by this device, plasma density (or ionization density) was calculated according to the equations

\[ N_\infty = \frac{4}{e A_p} \frac{I_{\nu}}{\bar{V}_e}, \]  

\[ N_m = \frac{\pi}{A_p} \left( \frac{Sm}{2e^2} \right)^{1/2}, \]

where \( N_\infty \) and \( N_m \) are the plasma and electron densities, respectively, \( I_{\nu} \) is the current at saturation (e.g. calculated from the I-V curve as shown in Figures 3a and 3b), \( A_p \) is the exposed surface area of the probe, \( A_e \) is the number of collected charged particles, \( \bar{V}_e \) is the average speed of electrons, \( S \) is the electron flux, and \( m \) and \( e \) are the mass and the charge of electron. The electron temperature \( T_e \) was estimated based on the derivative I-V curves (as e.g. in Figure 3b), according to the equation

\[ \ln \left( \frac{I_{\nu}}{I_{\nu}} \right) = \frac{e}{kT_e} \left( V - V_{pe} \right), \]

where \( I_{\nu} \) is the electron current, \( k \) is Boltzmann's constant, \( V \) is the external bias voltage, and \( V_{pe} \) is the plasma potential. The expressions (1-3) are simplifications derived for the Langmuir probe within so-called Thin Sheath Theory (Eqs. 1 and 3) and Thick Sheath Theory (Eq. 2).  

Plasma treatment

The plasma treatment was performed in a special UHV preparation chamber attached to the analysis chamber (see below). The C18/Au and C18/Ag samples were fixed on the sample holder in front of the outlet of a quartz tube (inner diameter of 5 mm) leading to the plasma glow discharge chamber (see Figure 1). The distance between the sample surface and this region was about 170 mm and between the sample and nozzle head about 10 mm. The glow discharge microwave plasma was produced using a microwave (~2.45 GHz) plasma generator OPTHOS Instruments Inc. ) with a power of 80 W. A flow rate of 500 sccm for N₂ gas (purity of 99.9999 %) was maintained by keeping a pressure of ~1 torr in the plasma processing chamber. The pressure in the gas-discharged region was about 13 torr.

The C18/Au and C18/Ag samples were simultaneously exposed to the afterglow plasma for either 2 min or 4 min. Note that although the plasma basically consisted of afterglow plasma, there was a portion of oxygen-derived species (presumably free radicals) originated from the walls of the preparation chamber and plasma-pathway tube.

X-ray Photoelectron Spectroscopy analysis

The characterization of both the pristine and plasma-treated AT films was performed by high-resolution X-ray photoelectron spectroscopy (HRXPS). Measurements were carried out at the U5 undulator beamline of the Synchrotron Radiation Research Center in Hsinchu, Taiwan. The energy resolution was 0.2-0.3 eV. The energy scale was referenced to the pronounced Au 4f½ “bulk” peak (84.00 eV) of the C18/Au sample. The energy calibration was performed for every sample and after every change of the photon energy to exclude effects related to the instability of the monochromator. Special care was taken to avoid the X-ray radiation-induced damage during the spectra acquisition.
The spectra were fitted using Doniaich-Sunjic peak profiles and Shirley background. To fit the S 2p\(\nu_{1}/2\) doublet we used a pair of such peaks with the same FWHM, the standard spin-orbit splitting of ~1.2 eV (verified by the fit) and the branching ratio of 2:1 (S2p\(\nu_{1}/2\)/S2p\(\nu_{3}/2\)). The resulting accuracy of the BE/FWHM values given in this letter is ~0.05 eV for both the S 2p and C 1s peaks.

Result

Pristine C18/Au and C18/Ag and plasma-induced changes

The S 2p, C 1s, and O 1s HRXPS spectra of the pristine (a) and the plasma-treated (b,c) C18/Au samples are presented in Figures 3, 5, and 7, respectively. The corresponding spectra for C18/Ag are depicted in Figures 4, 6, and 8. The N 1s HRXPS spectra of the plasma-treated C18/Au and C18/Ag samples are shown in Figure 10.

For the pristine films no traces of oxygen and nitrogen were found. The S 2p spectra exhibit a single S 2p doublet with BEs (S 2p\(\nu_{1}/2\)) of 162.09 eV and 161.98 eV for C18/Au and C18/Ag, respectively. The observed doublet is commonly related to the thiolate species bonded to the gold surface. The C 1s spectra of the pristine AT films in Figures 6a and 7a exhibit a single emission peak at 284.8 eV for C18/Au and 285.2 eV for C18/Ag with identical FWHMs of ~0.9 eV in good agreement with previous XPS and HRXPS studies.

The plasma treatment results in noticeable changes in the S 2p and C 1s HRXPS spectra of both C18/Au and C18/Ag and in the appearance of the characteristic traces of oxygen and nitrogen in the O 1s and N 1s spectra. To follow these changes the respective spectra in Figures 3-9 are decomposed to the individual spectral components related to the definite chemical moieties in the plasma-treated films. A quantitative evaluation of the spectra decomposition is presented in Tables 1 and 2.

Discussion

The plasma processing of the C18 SAMs on Au and Ag substrates results in essential damage and disordering of the initially well-ordered and chemically homogeneous monomolecular layers. The most noticeable processes are partial desorption of hydrogen and carbon-containing fragments and subsequent cross-linking within the residual layer, partial oxidation of the alkyl matrix, appearance of the nitrogen-containing entities, and cleavage of the sulfur-substrate bonds with simultaneous (presumably) oxidation of the evolving sulfur species. Considering that the majority of the chemical transformations are mediated by oxygen and that the amount of the nitrogen-containing moieties in the plasma-treated C18 films is rather small (as compared to the oxygen-containing moieties, one can conclude that the oxygen-derived constituents in plasma provide the major impact. Assuming that our plasma consists to a greater extent from the nitrogen-derived entities, this finding is a new, very impressive manifestation of the extreme chemical activity of oxygen-derived plasma constituents such as O and O\(_2\) radicals and atomic oxygen.

Comparing the result of the plasma exposure for C18/Au and C18/Ag, we found that whereas the damage of the alkyl matrix in the both films is similar (even if the respective processes are somewhat slower in C18/Ag), the cleavage of the head-group-substrate bonds and the oxidation processes at the SAM-substrate interface evolve with a smaller rate and to a much lesser extent in C18/Ag than in C18/Au. This behavior implies that the reactions of the alkyl matrix and the S-substrate interface towards plasma processing are only partly correlated and that the S-substrate bond in C18/Ag is noticeably stronger than that in C18/Au. As to the above-mentioned partial correlation, it can be assumed that the remaining strong anchoring to the substrate after two minutes of the plasma treatment of C18/Ag (Figure 4b) is the reason for a smaller damage of the alkyl matrix in this system (Figure 6b). Alternatively, the almost completely oxidation of the pristine thiolate species at the S-Au interface in C18/Au after even a short plasma exposure (Figure 3b) is accompanied by an extended damage of the aliphatic matrix (Figure 5b). Note that along with the anchoring to the substrate there is another factor, which also affects the rate and extent of the plasma-treatment-related damage in aliphatic matrix of
C18/Au and C18/Ag, namely different packing densities of the alkyl chains, this parameter being larger in the latter system. However, we assume that the anchoring to the substrate has the major impact, given the relatively small value of this difference and similar damage of the alkyl matrix in C18/Au and C18/Ag.

As to the mentioned difference in the reaction of the S-substrate bond in AT/Au and AT/Ag towards the plasma treatment, similar phenomena were observed at the exposure of AT SAMs on gold and silver substrates by middle-energy (800 eV) He⁺ ions, low-energy (10 eV) electrons, and UV light in the presence of air. The same conclusions on an enhanced strength of the S-substrate bond in AT/Ag as compared to AT/Au have been derived. Additionally, this difference was considered to be the main reason for the dissimilar character of thermal desorption of ethanethiol from Ag(110) and Au(110) surfaces, where sulfur-containing species were released from Au, while an almost complete retention of sulfur could be observed on Ag.

Whereas some of the processes occurring during the exposure of AT SAMs to the nitrogen-oxygen plasma also takes place at the irradiation of these films by X-rays, electrons, and ions (e.g. partial desorption and cross-linking effects), the entire variety of the changes evoked by the plasma treatment in these systems has most close resemblance to the damage occurred at UV photooxidation. Considering that the damage at the UV exposure in the presence of air is predominately provided by the oxygen-derived reactive species generated by the UV light, this resemblance supports our conclusion that the atomic oxygen and oxygen radicals provide the major impact in the case of the plasma treatment described in this article. The appearance of the alkylsulfide species, (a BE of S 2p of 163.14 eV), typical for X-ray- and electron-induced damage and a relatively large downwards shift of the C 1s peak (0.5 eV vs. ~0.1 eV for C18/Au in this study) do not occur in our case, which agrees with the results of the plasma characterization (Section 3.1) implying a low density and low kinetic energy (most important) of the electrons and ions. At least for electrons, this energy (~0.5 eV) is not sufficient for the dissociative excitation of the individual bonds within the plasma treated films. Thus, the observed modification of the C18 SAMs should be mostly representative for the effect provided by the oxygen radicals.

These radicals seem to be even more reactive than the chemically active oxygen-derived species generated by the UV-light. Whereas an almost complete resemblance between the processes occurring at the S-substrate interface at the UV photooxidation and the plasma exposure can be assumed (based on the similarity of the respective S 2p spectra), a partial oxidation of the alkyl matrix (see Figures 5 and 6) does not take place in the case of the photooxidation. On the other hand, these oxidation processes can be at least partly related to the appearance of free radicals in the plasma treated films mediated by a small fraction of "hot" ionizing particles (electrons and ions), which is still present in a low-energy plasma. The amount of these particles is probably not enough to compete with the oxygen radicals at the S-Au interface, but probably adequate to participate to some extent in the oxidation of the alkyl matrix.

Based on the results of the UV photooxidation studies, we can assume that the rate-determining step in the photooxidation of C18/Au is penetration of oxygen radicals to the Au-S interface, while reactivity on Ag is dominated by S-C bond scission. Of course, a higher lateral packing density of the alkyl chains in C18/Ag (as compared to C18/Au) should somewhat slow down this penetration in C18 SAM on Ag. However, this small difference (18.4 Å for AT molecule in AT/Au vs. 21.3 Å in AT/Ag) cannot fully explain for the observed large difference in the extent and rate of the bond-scission and oxidation processes at the S-substrate interface in C18/Au and C18/Ag.

Conclusion

Synchrotron-based high-resolution photoelectron spectroscopy was applied to study the modification of the alkanethiol SAMs on gold and silver substrates by nitrogen-oxygen downstream microwave plasma. Although our initial intention was the use of a solely nitrogen plasma, we have not succeeded to avoid the appearance of the oxygen-containing contaminations in the plasma flow.

The characterization of plasma by a Langmuir probe exhibited a low density and low kinetic energy of the ionizable plasma constituents, such as electrons and ions. It was therefore assumed that the long-lived nitrogen and oxygen radicals provided the major impact of the plasma treatment.

It was found that such a treatment results in essential damage and disordering of the initially well-ordered and chemically homogeneous monomolecular AT layers. The most pronounced processes are the complete (C18/Au) or partial (C18/Ag) oxidation of the pristine thiolate species, partial desorption of hydrogen and carbon-containing fragments with subsequent cross-linking within the residual hydrocarbon layer, and partial oxidation and appearance of the nitrogen-containing entities in this layer. The plasma-treatment-induced
processes in the alkyl matrix and at the S-substrate interface are only partly correlated.

The rate and extent of the oxidation processes at the S-Au interface are noticeably smaller for C18/Au as compared to C18/Ag. In particular, almost no thiolate species become damaged or oxidized after a short (2 min) plasma treatment of C18/Ag, whereas the major part of the analogous species in C18/Au was found oxidized after the same plasma exposure. This suggests a stronger S-metal bond in AT/Ag.

The damage of the alkyl matrix in C18/Ag occurs somewhat slower than the respective process in C18/Au, which was explained by the different rate and extent of the oxidation process at the S-substrate interface in C18/Au and C18/Ag and by the difference in the packing density and orientational order of the alkyl matrix in these two systems.

The observation of a large portion of the oxygen-containing moieties in the plasma treated films and the comparison of the changes caused by the plasma treatment in AT SAMs with the processes occurring at the exposure of these systems to X-rays, electrons, or UV light (in the presence of air) imply that the major effects are provided by the oxygen radicals in agreement with the results of the plasma characterization. The results of this study show that a smallest oxygen contamination should be avoided if one wants to perform a soft modification of thin organic layers or definite molecular entities attached to these layers through a plasma treatment. The future work should include such an option as well as a better control of the plasma composition and parameters of the plasma constituents. Complementary information can be also provided through the variation of the parameters of the plasma-treated organic films. The first experiments on the thioaliphatic SAMs are on the way.

Reference


Figure 1

1. Tungsten wire diameter 0.25mm length 50mm
2. PTFE tape
3. Quartz tube
4. Ag wire
5. PTFE
6. Cu electrode
Table 1
Quantitative evaluation of C 1s peak intensities for the pristine and plasma-treated C18/Au and C18/Ag (see Figures 5 and 6). \(N_{\text{C1s}}\) and \(N_{\text{C1s\,main}}\) are the entire C 1s intensity and the intensity of the main C 1s emission at 285.1-284.8 eV, respectively (the BEs of the C 1s peak are different for C18/Au and C18/Ag; there is a downward shift of these values upon the plasma treatment, see text). The intensity ratios of the pristine films have been taken as 1.00.

<table>
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<th>Intensity ratio</th>
<th>(N_{\text{C1s}}/N_{\text{Ag}})</th>
<th>(N_{\text{C1s,main}}/N_{\text{Ag}})</th>
<th>(N_{\text{C1s}}/N_{\text{Ag,main}})</th>
<th>(N_{\text{C1s,main}}/N_{\text{Ag,main}})</th>
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<tr>
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Table 2
Quantitative evaluation of the O 1s and S 2p peak-intensities for the pristine and plasma-treated C18/Au and C18/Ag (see Figures 3, 4, 7 and 8). \(N_{\text{O2p}}\) and \(N_{\text{S2p}}\) are the entire S 2p and O 1s intensity, respectively. All ratios for Au and Ag substrates are normalized to the \(N_{\text{C1s}}/N_{\text{Ag\,main}}\) and \(N_{\text{C1s}}/N_{\text{Ag\,main}}\), respectively (see Table 1).

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<tr>
<th>Intensity ratio</th>
<th>(N_{\text{O2p}}/N_{\text{Ag}})</th>
<th>(N_{\text{S2p}}/N_{\text{Ag}})</th>
<th>(N_{\text{O2p}}/N_{\text{Ag,main}})</th>
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