Plasma-enhanced Acrylic Acid Vapor-grafted onto the Alkanethiolate Metal Surface Examined by Synchrotron Source X-ray Photoelectron Spectroscopy

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Abstract

This work utilizes synchrotron light source to study self-assembled monolayers (SAMs) using thiols \((\text{HS-}\left(\text{CH}_2\right)_n\text{CH}_3)\) as sulfur anchor group from solution onto Au (111) or Ag (111) surface. On the alkylthiolate (AT) SAMs surface, low ionization density of N\textsubscript{2} downstream microwave plasma \((1.5\times10^8 \text{ N.cm}^{-3})\) creates activated alkyl chains, meanwhile, affects diversely to S/Au and S/Ag interfaces. The AAc (Acrylic Acid) monomer is then introduced through diluted and vaporized phase with N\textsubscript{2} as the carrier gas; the consistency is 5\% AAc. This 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 both plasma species and the neighboring oxygen, the C-O, C-N and C=O bonds can be found. Such N, O-containing structures mostly result from chemical reactivities of free radials in plasma. The AAc monomers are reactive with activated alkyl chains, the presence of C 1s at 289.5 eV (O-C=O) are regarded as the evident of AAc grafting on the modified AT SAMs. Sulfur anchor onto Ag (111) surface is much resistant to the reactive plasma species, compared with that onto Au (111) substrate; however, the alkyl chains on Ag (111) substrate are removed successively. Using the sessile drop method, the contact angle of the AT SAMs surface is \(\text{ca. } 110^\circ\), compared with almost completely wetted \((71.5^\circ)\) AAc-grafted AT metal surface. This also indicates the occurrence of interfacial reactions between the alkyl chains and the AAc monomer.

Keywords: alkylthiolate surface, N\textsubscript{2} plasma. Acrylic acid, Interfacial reactions.
1. Introduction

Synchrotron based high-resolution photoelectron spectroscopy was applied to study the modification of the alkanethiol (AT) self-assembled monolayers on gold and silver substrates by nitrogen-oxygen downstream microwave plasma and vapor acrylic acid grafting. A major reason for the rather restrained activities concerning the plasma treatment of SAMs is presumably a large complexity of the physical and chemical processes occurring during the interaction of plasma with these systems. Both the ionizing species such as ions, electrons, free radicals, and the UV-light generated by plasma affect a SAM film at the same time. Considering that the plasma composition and the energies of plasma constituents depend upon the type and mode of generation\textsuperscript{18,41} and taking into account that every of these constituents interacts with a SAM in its specific way, one is confronted with a very complex situation. The problems can be, however, simplified if at least a partial characterization of plasma is performed and a well-established SAM system is taken. The choice of AT SAMs as an object of the plasma treatment is related to the large popularity of these systems, which probably are the best studied SAMs by present and are often used as model SAM films.\textsuperscript{2} The chainlike AT molecules are bonded to the substrate via their sulfur head group forming a a(4×2) modulated commensurate (√3 × √3) R30° lateral lattice on Au(111) surfaces and an incommensurate (√7 × √7) arrangements on the Ag(111) substrates.\textsuperscript{1,46-49} The resulting larger packing density in AT/Ag is accompanied by a smaller inclination of the AT chains as compared to AT/Au: The average tilt angles of AT chains in AT/Ag and AT/Au are 10-12° and 27-33°.\textsuperscript{1,12,46} Additionally, there are some indications for the different strengths of thiolate-substrate bonding for these two systems,\textsuperscript{46,50} namely for a stronger thiolate-substrate bond for AT/Ag as compared to AT/Au.\textsuperscript{3,22,51}

This work utilized synchrotron light to study self-assembled monolayers using thiols as sulfur anchor group from solution onto Au(111) or Ag(111) surface. With thiols bond surface, N\textsubscript{2} plasma is applied to create activated sites. The Aac monomer is then introduced through diluted and vaporized phase. The pAAc-grafted chains provide O=C-OH functional group. Subsequently, the coupling O=C-O may react with NH\textsubscript{2}-tail proteins or enzymes and form O=C-NH bonding, eventually for specific applications such as the sensing surface as biomedical receptors. This process and characterizations have been mostly carried out in a ultra-high vacuum chamber with sample transfer system. (SRRC-U5).

2. Materials

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\textsuperscript{54} and from the characteristic binding energy (BE) shift of the Au 4f surface component\textsuperscript{55}. The SAMs were formed by immersion of the substrates in an ethanolic 1mM solution of octadecanethiol [C\textsubscript{18}: CH\textsubscript{3}-(CH\textsubscript{2})\textsubscript{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 C\textsubscript{18} SAMs (measured by sessile drop method) was found to be 108±2°, as could be expected for the hydrophobic CH\textsubscript{3} surface.
Plasma treatment

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 region (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 nitrogen-derived species, there was a portion of oxygen-derived species (presumably free radicals) originated from the walls of the preparation chamber and plasma-pathway tube.

Vapor Acrylic acid grafting

For the vapor-phase reactions, AAc (Acrylic Acid) was mixing in the mixing chamber (see figure 2). Using nitrogen as carry gas.
The vapor was let in for 4 min, during which time the preparation chamber was kept at 1.2 Torr by continuous pumping.

Water contact angle

Contact angles of water on the nitrogen-plasma treated and vapor Acrylic acid grafting C18/Au and C18/Ag surface were measured according to the sessile drop method. The measurement was carried out at room temperature. The volume of water drop were fixed at 2 μl. The contact angle was determined from average of five times measurements with a standard deviation of 1 degree.

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. For doing the HRXPS characterization the samples were directly transferred to the UHV analysis chamber attached to the preparation chamber and equipped with a CLAM-4 9-channel electron energy analyzer (VG Microtech). An excitation energy of 390 eV was utilized to measure the Au 4f, S 2p and C 1s core level spectra, while the Ag 3d, N 1s and O 1s spectra were acquired with a photon energy of 650 eV. 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 Doniach-Sunjic peak profiles and Shirley background. To fit the S 2p3/2,1/2 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 (S2p3/2/S2p1/2). 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.

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3. Result

Water contact angle measurement

C18/Au and C18/Ag were treated with the nitrogen afterglow plasma at microwave power of 80W, 4 min. Table 1 show typical result of the contact angle of water on the C18/Au and C18/Ag surface. The contact angles agree well with previous work. As shown in table 1, leads to large decrease in the contact contact angles within 4 min after exposing the C18/Au and C18/Ag surface to afterglow plasma.

Water contact angles between plasma treatment and plasma treatment with vapor AAC graf were almost the same.

X-ray photoemission spectroscopy

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 2p3/2) 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 3(1) and 4(1) 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 observed changes imply above all a decomposition and partial oxidation of the initially intact C18 chains. The downward shift and broadening of the main C 1s peak suggest a partial desorption of hydrogen and cross-linking in the plasma-treated films in the same fashion as it occurs for X-ray or electron irradiation. Note that whereas the BE positions of the C 1s emission for the pristine C18/Au and C18/Ag films were noticeably different (see above), their positions became approximately the same after the plasma treatment. Another general feature is a similar (by ~20% after 4 min plasma treatment) decrease of the joint C 1s intensity, which is associated with a partial desorption of the carbon-containing fragments or complete C18 chains, again in the same manner as it happens for the X-ray or electron irradiation. Generally, comparing the analogous spectra in Figures 5 and 6, one can conclude that the plasma treatment causes similar changes in the alkyl matrixes of these two films, although the respective processes evolve somewhat slower in the case of C18/Ag.

After 4 min plasma treatment and then evaporated acrylic acid, the characteristic O=C-OH for AAC was found in C18/Au (see figure 7). The N element was detectable. The O-containing chemistries were obviously increased owing to the inclusion of O=C-OH group.

Ag/thiols/4 min. N2 plasma-treated thiolate Ag surface similarly reacted with the evaporated acrylic acid (AAC, 5% AAC with 95% ultra pure N2) and projected to thiols-bonded Au. The characteristic O=C-OH for AAC was detectable. The S 2p spectrum did not show significant change of S 2p binding states. The N element was not found obviously. The O 1s intensity did not increased in spite of the inclusion of O=C-OH group. Analytical result implied that thiolate Ag surface was obviously resistant to plasma species; after the projection of plasma species plus AAC vapor, the activated sites at Ag/thiols surface were also reduced the binding capability with AAC.

Figure 9 show the spectra for plasma-induced chemistries on the thiolate Au surface: C 1s spectra, which showed that carbons reacted with O and N elements, the increase of O-containing groups were correlated with the inclusion of AAC. The binding states of sulfur were altered owing to the interactions among plasma species, AAC and thiols-bonded Au. Figure 10 show the spectra for plasma-induced chemistries on the thiolate Ag(111) surface: C 1s spectra, which showed little
modification for the carbon states of thiols after reactions with plasma species plus AAc monomer. Binding states of sulfur were slightly varied owing to the interactions between plasma species and Ag/thiols. Analytical result displayed that thiolate Ag surface was little affected by plasma species; whether plasma-activated sites capable to bind with AAc was not clear.

4. Discuss

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. 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. Capability to resist plasma species projection for SAMs using thiols as sulfur anchor group from solution onto gold or silver surface was different. Sulfur anchor Ag/thiols surface was relatively stable. Sulfur anchor Ag/thiols surface was resistant to plasma species; the activated sites were capable to bind with AAc monomer. The tilted angles and binding density of thiols to Au (111) and Ag (111) are different, which may arise dissimilarity in measuring the intensities of S 2p or the ratio of bound thiols on the surfaces.

Reference


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<td>C18/Ag</td>
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**Figure 1**

**Figure 2**

**Figure 3**