

Control Over Surface Properties Through Modification of Monomolecular Films

The control of the surface behavior of materials on macroscopic and microscopic length scales is fundamental for progress in many fields of science and technology, such as chemistry, medicine, biology, and microelectronics. An universal approach to tailor the properties of surfaces and interfaces is their passivation by self-assembled monolayers (SAMs), which are well-ordered and densely packed 2D-ensembles of long-chain molecules, chemisorbed onto a substrate by a suitable headgroup, e. g., aliphatic and aromatic thiol-derived SAMs, as shown in Fig. 1. The

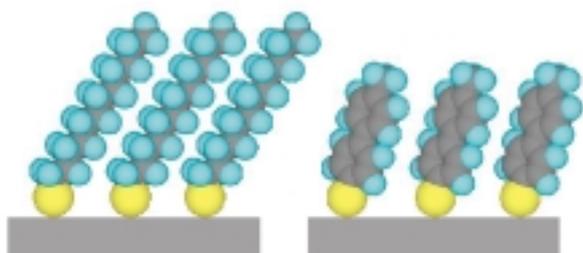


Fig. 1: Aliphatic and aromatic thiol-derived SAMs. The molecules are bonded to a substrate by the sulfur headgroup (yellow). An alkyl chain or an aromatic chain build the molecular spacer (carbon - grey, hydrogen - blue). In the given example both SAMs are terminated by the methyl group. Other functional groups can be attached and the molecular spacer can be modified.

flexible molecular architecture and a broad variety of the SAM building blocks allow to adjust and to control fundamental processes such as wetting, lubrication, corrosion, adhesion, and protein affinity. An additional option for tailoring the surface properties is physical modification of

SAMs by irradiation with electrons, X-rays, UV light, and ions, or plasma treatment.

The kind of changes induced by physical modification can be controlled through the molecular structure of the SAM constituents. In particular, it was recently shown that aliphatic and aromatic SAMs react differently towards electron irradiation. Whereas for aliphatic SAMs electron irradiation causes bond cleavage and disorder, a quasi-polymerization with only partial disordering occurs in aromatic SAMs. Applying an electron beam writer or performing the irradiation through a mask, lithographic patterns on micrometer and nanometer length scale have been fabricated with aliphatic and aromatic SAMs serving as a positive resist or negative resist, respectively. In addition, the resistance of the aromatic SAMs towards electron irradiation allows attachment and subsequent selective, chemical modification of terminal functional groups, which enables the fabrication of *chemical* lithographic patterns and templates. The fabricated lithographic patterns can then be used for the laterally selective attachment of other molecules or biological objects, such as proteins or cells.

Whereas the fabricated lithographic structures and chemical patterns can be visualized by SEM and AFM, a spectromicroscopic characterization of the patterned SAMs or an imaging based on the chemical identity of the SAM patterns has not yet been performed. To overcome this shortage, we have applied soft X-ray scanning photoelectron microscopy (SPEM) to image and characterize molecular patterns produced by electron irradiation of various aliphatic and aromatic thiol-derived SAMs through masks with 10 μm and 1.6

μm openings. The measurements were carried out with the SPEM end station located at SRRC's U5 beamline.

The Au 4f and C 1s SPEM images of the C16/Au (Cn: $\text{CH}_3(\text{CH}_2)_{n-1}\text{SH}$) and NPBT/Au (NPBT: $\text{NO}_2(\text{C}_6\text{H}_4)_2\text{SH}$) films after exposure to 300 eV electrons through the masks are presented in Fig. 2. The fabricated patterns can be clearly

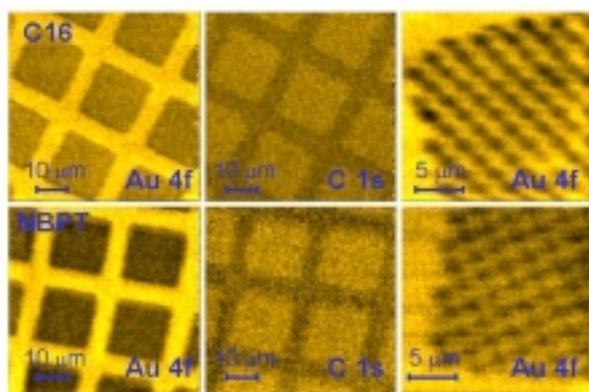


Fig.2: Au 4f and C 1s SPEM images of the electron-beam patterned aliphatic and aromatic SAMs. The patterns in the right images are circular dots with a diameter of $2\ \mu\text{m}$ arranged in quadrates. Whereas the mesh-like patterns (left, center) are clearly resolved, the smaller circular dots (right) are smeared, which is related to a limited lateral resolution of the photoelectron microscope.

identified and the inverse contrasts for the Au 4f and C 1s images suggest that the goal of the "chemical" imaging has been achieved. Interestingly, contrary to the initial expectations, the thickness of the films in the irradiated areas appears larger than that in the non-irradiated ones, as the former areas reveal a smaller Au 4f intensity and a higher C1s signal. This can be explained by adsorption of the airborne carbon-containing molecules on the irradiated areas. An enhanced affinity of these areas to the airborne molecules is presumably related to the presence of chemically active sites and a high roughness.

In addition, N 1s and F 1s images of the patterned NPBT/Au were acquired to monitor the irradiation-induced transformation of the nitro ($-\text{NO}_2$) tail groups into amino ($-\text{NH}_2$) ones and the subsequent attachment of trifluoroacetic acid

anhydride (TFAA) to the latter moieties (some of the patterned NPBT/Au were immersed into a TFAA solution). The collected images were found to mimic the Au 4f ones, which is explained by the low intensity of the N 1s and F 1s emissions assigned to the nitro and amino functions and TFAA molecules relative to the inelastic background dominated by the gold signal. A way to reduce the background problem is to collect a large amount of counts in every image pixel with the subsequent subtraction of the out-of-the-emission images from on-the-emission ones. However, this approach was found to be not applicable in the present case, because of irradiation-induced damage caused by the SPEM-focused X-ray beam during the image acquisition. In particular, a non-damaging recording of high-resolution photoelectron spectroscopy (HRXPS) spectra from the patterned areas was only possible after a complete defocusing of the beam (a reduction of the flux by a factor of ~ 150). Even under these conditions, it took only ~ 10 min to modify the sample, as indicated by the changes of

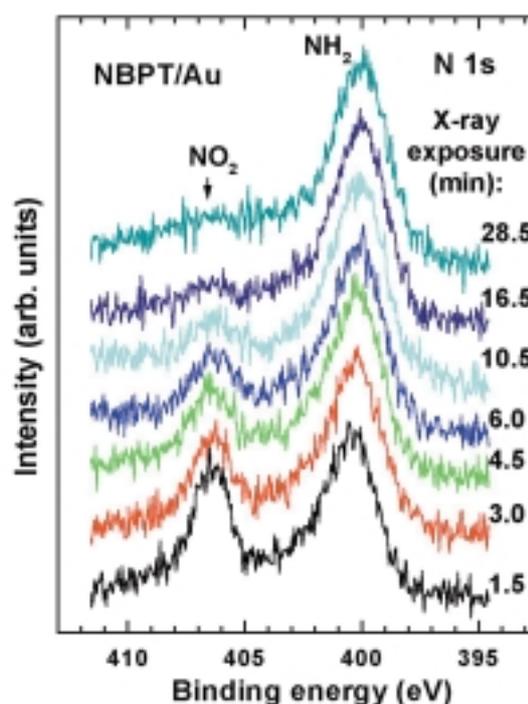


Fig.3: A series of successive N 1s HRXPS spectra acquired from the electron-beam patterned NBPT/Au with defocused primary X-ray beam. The duration of the X-ray exposure is marked at the respective spectra.



the N 1s HRXPS spectra (Fig. 3).

Besides electron-beam patterning of SAMs, we studied another important approach to modify these systems - plasma treatment. Whereas this method is widely applied in microelectronics for chemical modification, etching, and patterning of organic surfaces and thin organic films, there are only few examples of respective studies with ultrathin molecular films, such as SAMs. A major reason for the rather restrained activities in this field is presumably the complexity of the physical and chemical processes occurring during the interaction of the plasma with organic systems. Both ionizing species such as ions, electrons, free radicals, and UV-light generated by plasma interact with the sample simultaneously. To minimize the complexity, we applied a well-characterized nitrogen-oxygen downstream microwave plasma, in which the effect provided by electrons and ions can be neglected because these plasma constituents have a too low energy to affect the films. Under these conditions, the major impact is caused by chemically active atomic species and radicals in the plasma. Different aliphatic and aromatic thiol-derived SAMs on gold and silver substrates were chosen as test systems. The chemical changes and desorption processes in the plasma-treated SAMs were monitored by HRXPS on the spectroscopy branch of SRRC's U5 beamline.

It was found that the plasma treatment does not result in a "soft" modification of SAMs, but in their massive damage and disordering. Contrary to the electron beam treatment, both the aliphatic and aromatic films became modified and damaged in a similar way, with the extent of the changes depending on the length of the molecular chains and, above all, on the substrate, as demonstrated by Fig. 4. For SAMs on Au, a profound desorption of the entire SAM constituents and a complete fragmentation of the residual hydrocarbons is observed. For the SAMs on Ag, only partial desorption and oxidation took place and, for short treatment times, the films remained practically intact. The desorption of molecular species is preceded by the oxidation of the pristine thiolates to weakly-bonded sulfones (see Fig. 5), which occurs after the penetration of chemically active

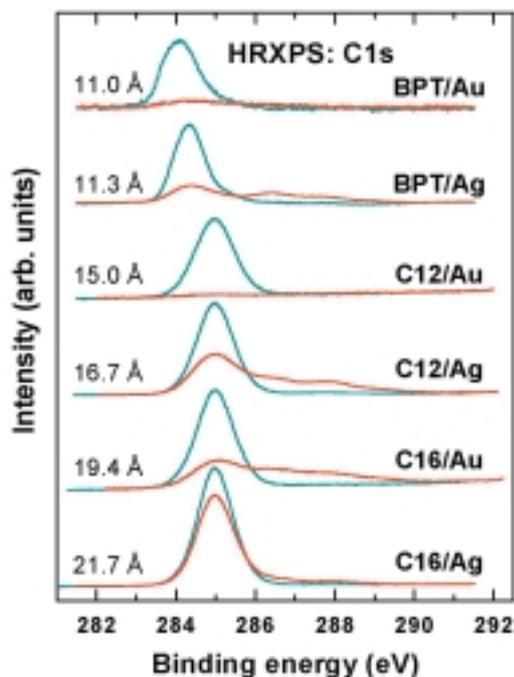


Fig.4: C1s HRXPS spectra of pristine (blue) and plasma-processed (red: 3 min for C12 and C16, 4 min for BPT) BPT, C12, and C16 SAMs on Au and Ag. The SAM thickness is marked at the respective spectra. The decrease of the entire C 1s intensity (desorption) and the appearance of new emissions at higher binding energy (oxidation) can be clearly followed.

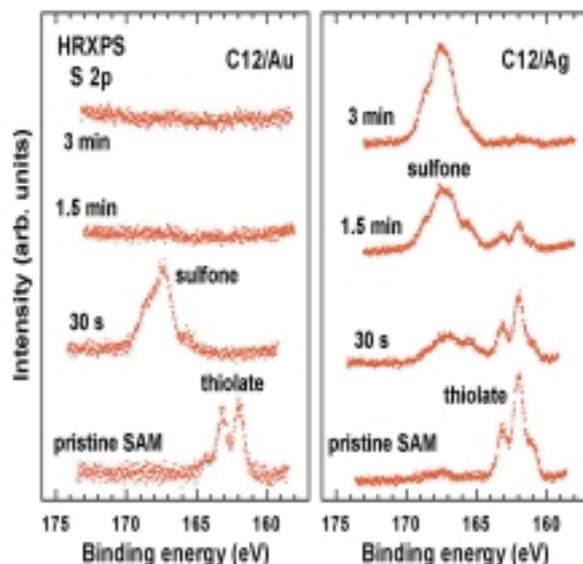


Fig.5: S 2p HRXPS spectra of pristine and plasma-processed C12/Au and C12/Ag. The duration of the plasma exposure is marked at the respective spectra. The transformation of the pristine thiolate species into sulfone moieties and their subsequent desorption can be clearly followed.

oxygen species into the S/substrate interface via defect sites. Such a mechanism clearly explains the observed dependence of damage extent on the SAM thickness and emphasizes the importance of the strength of the thiolate-substrate bond. Thus, a stronger thiolate-substrate bond can be suggested for Ag as compared to the Au substrate.

In summary, we have succeeded in chemical imaging of the electron-beam patterned aliphatic and aromatic thiol-derived SAMs and observed a contrast indicating adsorption of airborne carbon-containing molecules on the irradiated areas. Imaging was found to be only possible for the rather intense emissions, otherwise an X-ray induced damage and the inelastic background hinder the observation of a chemical contrast. In the case of plasma treatment, the strength of the thiolate-substrate bond and the defect density were found to be of significance, and not the character of the long chain spacer (as in the case of electron irradiation). We believe that the differences in the response to plasma treatment for the SAMs on Au and Ag are mainly related to the stronger thiolate-substrate bond in the latter system. Considering the similarity of the plasma-induced processes and UV-photooxidation, one can extend the major conclusions obtained for the plasma treatment to UV-photooxidation.

Future activities should include a search for the optimal parameters to improve the sensitivity of SPEM imaging, SPEM characterization of the plasma-treated patterned SAM, and the attachment of the biological objects to the plasma-modified SAMs. A first successful example to fabricate the respective linkage was recently realized with BPT/Ag. A further interesting issue to be addressed is quantitative measurement on X-ray induced damage in thin organic films, i.e., cross-sections and their dependence on the photon energy. Also, the modification caused by the zone-plate-focused X-ray beam opens up the possibility of direct writing of lithographic patterns by the X-ray microprobe.

Beamline:

09A1, 09A2 U5 beamline

Experimental Stations:

SPEM end station

Surface analysis chamber of U5 microscopy project

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