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Facile Route to Ultraflat SAM-Protected Gold Surfaces by “Amphiphile Splitting”**

Pooja Gupta, Katja Loos, Alexander Korniakov, Chiara Spagnoli, Mary Cowman, and Abraham Ulman*

Self-assembled monolayers (SAMs) of organic molecules[1] have drawn much attention in recent years and find application in, for example, biosensors,[2] nanomaterials,[3] molecular switches.[4] The functioning of these devices depends, in many cases, on the surface properties of the SAM. These properties, including wetting and adhesion, result directly from properties of the groups at the SAM–air interface, the composition of the monolayers, and their packing. It is known that smoother surfaces typically result in more uniform and densely packed SAMs.[5]

One significant drawback of polycrystalline metal substrates is that important instrumental tools for characterizing thin films, for instance, scanning tunneling microscopy (STM) and scanning probe microscopy (SPM), do not provide useful images of SAM structures, because the molecular structure of these SAMs is intertwined with the topography of the substrate (typically gold). The use of substrates (especially Au and Ag surfaces) with smoothness on the atomic scale extending over an area of several micrometers is, therefore, a prerequisite for arranging molecules into targeted architectures.

Although SAMs are not known to be stable themselves, they are particularly useful in eliminating and controlling surface properties that favor the accumulation of contami-
mica surfaces that otherwise confound pattern replication. Lee et al. reported on the influence of surface topography on the stability of SAMs. They found that alkanethiolate SAMs on surfaces with higher area densities of grain boundaries oxidized within hours to days to the corresponding sulfonates and sulfonates, whereas those having lower area densities showed no apparent oxidation after two weeks.\(^{[8]}\)

There are a number of methods for the preparation of thin gold films, and the quality of the resulting gold surface depends on, for example, the annealing conditions, evaporation rates, and substrate types.\(^{[10]}\) When mica substrates are used, ultraflat gold and silver surfaces comprising well-defined (111)-oriented crystals can be grown. Even though the surface of these metal films consists of domains with smoothness on the atomic scale, the overall film is quite rough because the individual domains are small. A possible route for decreasing the overall surface roughness is to utilize the template-stripping (TS) technique. Here, the upper gold surface of a mica/gold plate is glued to a silicon or glass substrate, and the mica is “stripped away”. The gold is mechanically separated from the mica with or without the aid of a penetrating solvent to access the backside, smooth gold surface. This procedure produces large areas of the smoothest gold surfaces known to date.

After the first reports on these template-stripped surfaces,\(^{[9]}\) improved procedures were published,\(^{[9]}\) and the importance of these surfaces for the basic understanding of, for example, SAMs,\(^{[10]}\) the attachment of biomolecules, and the preparation of designed surfaces became obvious.\(^{[12]}\) Still, template-stripped ultraflat gold surfaces are not easy to make, as the interface between the glue and the gold surface must be stronger than the interface between the gold and the mica. The whole process somehow involves an uncontrolled mechanical separation, which can lead to repeated contamination with the bonding agent or detachment solvent. Common problems with the stripping procedure also involve imperfect stripping, which results in gold surfaces with mica residues still attached.

In this communication we report on a facile route to SAM-protected ultrasmooth gold surfaces that does not involve harsh mechanical shear on the lower gold/mica interface. Knarr et al. measured the adhesion of this smooth gold/mica interface by direct force measurement and their value \(F_{n}/R = 1800 \text{ mN m}^{-1}\)\(^{[9b]}\) proves that high forces are indeed necessary to separate the gold from the mica.

It is well known that layered silicate structures like mica can intercalate small molecules, which eventually swell the structure and lower the adhesion between the layers. In a similar approach, we utilize organothiol solutions to intercalate between the mica and the gold layer, thus lowering the adhesion between these two surfaces. In this way it becomes quite easy to remove the mica from the gold without leaving any residual mica. In fact, after about one hour the mica layer can be removed from the gold surface without any mechanical stress. Because the SAM is built in situ, the ultraflat gold surface is never unprotected, and, furthermore, will not be contaminated when it is taken out of the solution, which is also a common problem of the other approaches.

Freshly cleaved mica sheets were mounted in a vacuum evaporator ca. 15 cm above the gold source and annealed overnight in vacuum \(\approx 10^{-7} \text{ Torr}\) at 300°C with a halogen lamp heater. Gold was evaporated at a rate of approximately 1 Å s\(^{-1}\), and the resulting gold substrates were annealed in vacuum \(\approx 10^{-7} \text{ Torr}\) at 300°C for 18 h. After cooling to room temperature, the chamber was filled with nitrogen, and the substrates were removed without further precautions. Glass slides were glued to the gold surface (with ca. 10 µL epoxy glue), and the glue was cured overnight at about 150°C. The mica was stripped by submerging the mica/gold/glass sandwich in a 200-µm solution of the thiol in ethanol for about 1 h, after which the mica could be removed easily with tweezers. The resulting surfaces were washed repeatedly with ethanol, dried with a soft stream of nitrogen, and stored under nitrogen. For reference purposes, pure gold surfaces were also produced by traditional template stripping (with ethanol).

With this procedure SAMs of octanethiol (1), octadecanethiol (2), 4'-hydroxy-4'-sulfanylbiphenyl (3), 4'-trifluoromethyl-4-sulfanylbiphenyl (4), 4-methylsulfanyl-4'-sulfanylbiphenyl (5), and 4'-carboxethyl-4'-sulfanylbiphenyl (6)\(^{[13]}\) were produced. The thickness of these SAMs was estimated by ellipsometry. At least three individual points were measured on each sample, with an assumed refractive index of 1.462 for the organic film. The results (Table 1) are in a good agreement with the theoretical predictions and earlier results for perfect SAMs.\(^{[5,13]}\)

Static contact angles were determined at room temperature by the sessile-drop method. To measure the advancing and receding angles, we examined 5-µL droplets that were formed at the end of blunt-ended needle of a syringe. Advancing and receding angles were measured by tilting the sample stage. The stage tilt was increased until the droplet started to move on the surface, at which time the tilt was immediately decreased to a point at which the droplet stopped moving. Maximum advancing and minimum receding contact angles for water were found at a tilt angle of ca. 40°. Images of the droplet were analyzed with NIH software. The results (Table 1) agree well with literature values.\(^{[1,13]}\)

It becomes obvious that contact-angle hysteresis \((\Delta \theta)\) is significantly less than previously reported values (the lowest are ca. 5°) and in some cases practically disappear due to the increased smoothness of the underlying gold surface.\(^{[5,13]}\)

### Table 1: Contact angles and thicknesses for SAMs produced by thiol splitting.

| Substrate or SAM | \(\theta_i (\pm 0.5^\circ)\) | \(\theta_f (\pm 0.5^\circ)\) | \(\Delta \theta (\pm 1^\circ)\) | Thickness [Å] | Surface roughness [nm]\^a | Root mean square value.
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<tr>
<td>Au (111)</td>
<td>71°</td>
<td>71°</td>
<td>0°</td>
<td>–</td>
<td>0.340</td>
<td>(1.7)</td>
</tr>
<tr>
<td>1</td>
<td>109°</td>
<td>108°</td>
<td>1°</td>
<td>8</td>
<td>0.690</td>
<td>(0.5 \pm 0.2)</td>
</tr>
<tr>
<td>2</td>
<td>105°</td>
<td>104°</td>
<td>1°</td>
<td>20</td>
<td>0.377</td>
<td>(0.6 \pm 0.2)</td>
</tr>
<tr>
<td>3</td>
<td>31°</td>
<td>30°</td>
<td>1°</td>
<td>13</td>
<td>0.470</td>
<td>(0.6 \pm 0.2)</td>
</tr>
<tr>
<td>4</td>
<td>85°</td>
<td>81°</td>
<td>4°</td>
<td>13</td>
<td>0.362</td>
<td>(0.6 \pm 0.2)</td>
</tr>
<tr>
<td>5</td>
<td>70°</td>
<td>64°</td>
<td>6°</td>
<td>15</td>
<td>0.298</td>
<td>(0.6 \pm 0.2)</td>
</tr>
<tr>
<td>6</td>
<td>65°</td>
<td>64°</td>
<td>1°</td>
<td>15</td>
<td>0.610</td>
<td>(0.4 \pm 0.2)</td>
</tr>
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\(^{[a]}\) Root mean square value.
means that for the first time systematic wetting and adhesion studies can be conducted on molecularly engineered surfaces. With mixed SAMs it becomes possible to investigate the effect of surface chemistry on these important properties, and we already see these effects. For example, for the SAM prepared from 5, the surface is likely to be more disordered because of the expected distribution of dihedral angles between the methylsulfanyl group and the biphenyl moiety; the resulting contact-angle hysteresis is quite high (Table 1). Furthermore, by utilizing microcontact printing or E-beam lithography the effect of shape and size of the molecular layer on wetting and adhesion can be studied without the hindrance of surface roughness. Such studies are in progress in our laboratory.

Figure 1 shows the external reflection (ER)-FTIR spectrum of the octadecanethiol SAM on ultraflat gold produced by our approach. The spectrum is in very good agreement with those of crystalline SAMs. The SFM images (Figure 2) were recorded in the tapping mode. The amplitude of the SPM-etched silicon tip (TESP) was set ca. 1 V below the root-mean-square value). The roughness values are summarized in Table 1. The gold surfaces are composed of grains smaller than those in conventionally prepared surfaces (Figure 2a,b). Hence, if one needs micron-sized flat gold substrates (with one or two steps) for diffusion studies or determination of monolayer growth kinetics, these ultralat flat gold are not suitable, and rather very expensive gold single crystals are necessary. Thus, ultralat gold might be ideal for applications that require flatness rather than grain size, such as X-ray reflectivity, nanolithography, and interfacial phenomena such as wetting.

In conclusion, we have shown that self-assembled monolayers of both aliphatic and aromatic thiols can be produced with no apparent contact-angle hysteresis. This is accomplished by using the thiol solution as a splitting reagent for the removal of the mica from the gold surface in the template-stripping technique. These new smooth SAM surfaces open up opportunities for advanced studies of interfacial properties, including wetting and adhesion.

Experimental Section

Reagents and instrumentation: ruby mica sheets (commercial stove mica, Paramount Corporation, New York, USA); vacuum evaporator (Key High Vacuum); halogen lamp heater (Ushto Oregon Inc.); gold (purity 99.999%, Cerac); epoxy glue Epo-tek 377 (Epoxy Technology); Rudolph Research AutoEL ellipsometer (He-Ne laser, angle of incidence 70°); Ramé-Hart Model 100 goniometer, equipped with a high-resolution CCD-IRIS color video camera (Sony); drops were filmed with an Apple video player (Version 1.3.2), analysis with NIH Image (Version 1.57). ER-FTIR spectra were recorded on a Nicolet 760 spectrometer, equipped with an MCT-A detector with 2-cm	extsuperscript{-1} resolution (2048 scans), using a 80° fixed grazing-angle attachment (SpectraTech). IR (octanethiol SAM, see Figure 1): $\tilde{\nu} = 2962.9$ [v (CH$_3$, ip)], 2877.20 [v (CH$_3$, FR)], 2919.2 [v (CH$_2$)], 2835.0 [v (CH$_2$, FR)], 2850.1 cm	extsuperscript{-1} [v (CH$_3$)]. Nanoscope Multimode Scanning Probe Microscope (Digital Instruments, Inc.); silicon nitride tip (Nanoprobe, TESP).

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Keywords: gold · monolayers · self-assembly · surface roughness · thiols


