

X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS) imaging have been used to characterize the UV-irradiated and exchanged monolayers. XPS spectra of the S 2p region indicate the formation of sulfonate species upon UV irradiation and their displacement by thiolates following immersion. SIMS images of photopatterned and thiol-exchanged SAMs confirm the existence of two molecularly distinct assemblies with faithful reproduction of the mask pattern and resolution of features as small as 15 μm .

Any substrate on which a thiol SAM will form may be used in the invention. The substrate may take the form of a foil, a wafer or a chip of the desired material. Alternatively, particularly with precious metal substrate materials, it is desirable to use as the substrate a layer of substrate material deposited on a base material by any known deposition process. Suitable substrate materials include gold, silver, copper, platinum, iridium, palladium, rhodium, mercury, osmium, ruthenium, gallium arsenide, indium phosphide, mercury cadmium telluride, and the like. Gold and silver are particularly preferred.

The light pattern to which the thiol monolayer is exposed may be generated using any suitable source of electromagnetic radiation which will promote the oxidation in oxygen or air of a thiol group to a sulfonate group. Ultraviolet light of any wavelength or even x-ray radiation may be used. Particularly good results have been obtained using a mercury lamp as the light source.

The exposure and exchange steps may advantageously be carried out at ambient temperature, although higher or lower temperatures may be used. The exposure time required to oxidize the thiolate groups to sulfonate groups will vary depending on the layer density or thickness, the oxygen concentration and the intensity and/or wavelength of the applied radiation. For typical mercury vapor lamp, exposure times in air of 15 minutes to 1 hour or more may be used with good results. For any given case, persons skilled in the art can readily determine appropriate exposure times by simple testing.

The exchange time is not critical. Immersion times of as little as one minute or as long as an hour or more have yielded satisfactory results. Unduly extended immersion times for the exchange or developing step are preferably avoided, however, since they may increase the likelihood that the original thiolate compound in the unexposed regions may undergo exchange with the new thiolate compound of the exchange solution.

Exchange in unexposed regions can be limited by removing sulfonate species prior to immersing the exposed substrate in the solution of the new thiolate compound. Removal may be effected by means of a solvent such as ethanol, methanol, water, acetone, dimethyl sulfoxide, hexane, tetrahydrofuran or dimethylformamide, or by laser treatment or ion bombardment techniques.

Other objects, advantages and novel features of the present invention will become apparent from the following detailed description of the invention when considered in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a structural depiction of a single alkylthiol molecule;

FIG. 2 is a cross sectional view of a self assembled monolayer (SAM) deposited on a gold substrate;

FIGS. 3a-3c depict various steps of the photopatterning process according to the invention;

FIG. 4 shows an alternate embodiment of the invention in which a UV pattern is formed by projecting the mask pattern on the sample;

FIGS. 5a-5d depict the steps of the process according to the invention applied to control the placement of biological molecules on a surface;

FIGS. 6a and 6b are structural depictions of patterned biomolecular films formed according to the invention, and

FIGS. 7a-7b show SIMS images of a biological molecule adsorbed on a surface.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Thiolate self-assembled monolayers (SAMs) are well-defined monomolecular films that offer tremendous flexibility in tuning the chemical and physical properties of surfaces and interfaces. Such films can be formed from thiol molecules such as omega-substituted alkanethiols and disulfides. For example, alkylthiols or thiophenols may be used. Alkylthiol molecules, illustrated structurally in FIG. 1, correspond to the general formula $\text{R}-(\text{CH}_2)_n-\text{SH}$, where SH is the sulfur or thiol head group, n may represent any desired integer depending on the desired character of the layer to be formed, and R represents the terminal functional group (e.g., $\text{HOOC}-$, $-\text{CH}_3$, $-\text{NH}_2$, CF_3 , halogen, etc.). Typically n will range from 0 to 21. The group R may be any functional group which will confer a desired character on the SAM, depending on the intended use.

Other types of compounds which are capable of producing alkylthiolate monolayers and are useful in the invention include dialkyl sulfides and dialkyl disulfides.

Dialkyl sulfides correspond to the general formula $\text{R}(\text{CH}_2)_m\text{S}(\text{CH}_2)_n\text{R}'$ where R and R' may be any terminal functional groups, and m and n represent any desired integers. Typically m and n will range from zero to 21. Either symmetrical or asymmetrical dialkyl sulfides may be used. Examples of symmetrical dialkyl sulfides include $[\text{CH}_3(\text{CH}_2)_n]_2\text{S}$, $[\text{HOOC}(\text{CH}_2)_n]_2\text{S}$, $[\text{F}(\text{CF}_2)_m(\text{CH}_2)_n]_2\text{S}$ and the like where m and n have the meanings given above. Examples of asymmetrical dialkyl sulfides include $\text{CH}_3(\text{CH}_2)_9\text{S}(\text{CH}_2)_{10}\text{COOH}$, $\text{CH}_3(\text{CH}_2)_5\text{S}(\text{CH}_2)_{10}\text{COONa}$ and $\text{CH}_3(\text{CH}_2)_{15}\text{S}(\text{CH}_2)_{15}\text{COOH}$ and the like.

Examples of dialkyl disulfide compounds include symmetrical dialkyl disulfides such as $[\text{S}(\text{CH}_2)_n\text{OH}]_2$, $[\text{S}(\text{CH}_2)_n\text{CH}_3]_2$, $[\text{S}(\text{CH}_2)_n\text{Br}]_2$, $[\text{S}(\text{CH}_2)_n\text{COOH}]_2$ and the like, and asymmetrical dialkyl disulfides corresponding to the formula $\text{R}(\text{CH}_2)_m\text{S}-\text{S}(\text{CH}_2)_n\text{R}'$ where R and R' may be any terminal functional groups as describe above, and m and n have the meanings given above, with the proviso that R and R' may only be the same if m and n are different, and m and n may only be equal if R and R' are different.

The foregoing lists are merely representative examples, and there many other compounds which could be used in the invention. The important characteristic is the ability to form a thiolate monolayer on a substrate.

A monolayer is formed by immersing an appropriate substrate (such as gold, silver, copper, etc.) into a dilute solution of a compound capable of forming a thiolate group, such as an alkylthiol. For convenience in discussion, the following description will refer specifically to alkylthiol compounds, but it should be understood that any compound which is capable of forming a thiolate monolayer may be used in the invention.