

# Formation and *in Situ* Modification of Monolayers Chemisorbed on Ultraflat Template-Stripped Gold Surfaces

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We have previously described the preparation of ultraflat Au(111) surfaces as substrates for scanning probe microscopy. We report here alternative ways to produce polycrystalline Au(111) thin films of similar, high quality (i.e., with mean roughness smaller than 5 Å over 25 μm<sup>2</sup>). All of them are based on the same principle, i.e., that of exposing the very first layer of gold atoms which had deposited onto mica. One alternative route leads to substrates which are transparent enough for optical microscopy. Two other routes make use of ceramic glues, providing substrates which can be handled with most organic solvents without disruption of the Au(111) layer. The substrates prepared by the latter procedures can thus be used to produce gold-directed self-assembled monolayers (SAMs) from nearly all ω-functionalized alkanethiols or dialkyl disulfides; they can also be used for the *in situ* chemical modification of SAMs on gold. For this purpose, appropriate reaction chambers have been developed. As an example of the use of the new techniques described here, we report the preparation of a SAM of *N*-palmitoylcysteamine, either from *ex situ* synthesis of the precursor or from *in situ* acylation of the amino head groups of a cysteamine SAM.

## Introduction

Scanning tunneling microscopy and atomic force microscopy are now well-established analytical methods in solid state physics and materials science. They are also becoming more and more important tools in structural research in biology and organic chemistry, as demonstrated by the increased number of publications in these fields which have appeared in the last few years.<sup>1-6</sup> However, scanning probe microscopy (SPM, as these and related techniques are collectively designated) has not yet become routine with sensitive samples such as biomolecules or organic structures; i.e., the research in this field is still focused on several methodological aspects.

Chemical and physical properties of the substrate are of primary importance. In addition to being chemically well defined and inert against O<sub>2</sub>, yet endowed with specific chemical reactivity, the substrate must be atomically flat over large areas; if not, objects having unfavorable length: width ratios will "sink" into an irregular topography. This is especially true for fibrillary structures of μm in length, e.g., nucleic acids or organic polymers with diameters smaller than 3 nm, but holds true also for individual globular proteins. These macromolecules require substrates with a mean roughness as small as a few angstroms on areas of at least 5 μm<sup>2</sup>.

Substrates of very low roughness are advantageous also for the formation of self-assembled monolayers (SAMs) and in the investigation of phenomena such as adsorption, adhesion, wetting, lubrication, or friction. Finally, the

ideal substrates should also be reasonably priced and easy to prepare, to store, and to chemically modify.

Gold is becoming a popular substrate. For most purposes its surface is satisfactorily inert, but can easily chemisorb dialkyl disulfides or alkanethiols, which spontaneously organize into regular SAMs.<sup>7-11</sup> In addition, if ω-functionalized, these monolayers should in principle allow a variety of novel and sophisticated molecular architectures. Gold surfaces thus have the potential of being important tools in the expanding field of SAMs for chemical sensing, nonlinear optics, and lithography.<sup>12</sup>

Several procedures have been reported which yield atomically flat gold terraces over several 100 nm.<sup>13-16</sup> The quality of these surfaces, (i.e., flatness over large areas) generally lags behind that of mica, however. With the ultimate goal of preparing ω-functionalized bioreactive SAMs on gold in order to image immobilized biological structures by SPM, we have recently developed a procedure to prepare Au(111) surfaces with a mean roughness of 2-5 Å on areas of at least 25 μm<sup>2</sup>.<sup>17</sup> Briefly (see Figure 1A): gold is first grown epitaxially onto mica (which is among the flattest surfaces known); the gold layer is then glued onto a silicon wafer and the mica is stripped off. The uncovered, template-stripped gold surface (TSG) (i.e., the very first atom layer of gold having deposited onto the mica) is nearly as flat as mica itself but has the favorable chemical properties of gold. On these ultraflat, polycrys-

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