

## **Gold Substrate Preparation**

High quality, clean gold substrates are needed to produce high quality SAMs and for obtaining consistent results. Gold coated substrates are most commonly prepared by evaporation, sputtering or plating of gold onto the substrate material of choice. Typical substrates consist of glass microscope slides, glass cover slips, quartz cover slips, mica and silicon. Many factors influence the quality of gold coated substrates and consequently the quality of the resulting self-assembled monolayers. These factors include the gold purity, substrate's roughness, cleanliness, coating method, and the treatment of the coated substrates after preparation.

### ***Substrates before Gold Coating***

#### ***Substrate Size***

The size of the substrate material will be dictated by the analytical instrument used to characterize the SAM or by the needs of future experiments. Other factors that may affect substrate size are the size of the self-assembly vessel, the amount of available alkanethiol for the sample preparation, and the volume of solution used.

For many typical surface analysis methods and applications, 1 cm x 1 cm samples are adequate. For applications requiring smaller samples than the available substrate material, the material will have to be cut. Two cutting choices are available: cutting before gold deposition or after. It is best to resize the substrate prior to depositing gold to prevent scratching of the gold surface and minimize contamination due to excessive handling.

#### ***Substrate Pretreatments***

Before gold deposition, it is typically necessary to clean the substrate material. Cleaning is necessary to remove oils, fingerprints, and other contaminants which are commonly found on materials due to processing and handling. It is recommended to clean the uncoated substrates even if they come "clean" from the supplier. It is important to keep the substrates separated from each other to prevent scratching during cleaning.

Possible cleaning protocols include:

#### ***A) Cleaning using a Solvent Rinse***

Substrates can be cleaned using a series of water and solvent rinses.

1. Soak samples in a large volume of water overnight to remove adsorbed salts. (This step can be omitted if no salts are present).
2. Sonicate samples in methylene chloride for 5 minutes. Repeat once with fresh methylene chloride.
3. Sonicate samples twice in methanol, 5 minutes each time, using fresh solvent.
4. Sonicate samples twice in acetone, 5 minutes each time, using fresh solvent.
5. Dry samples with a stream of N<sub>2</sub>.

### ***B) Cleaning using Piranha Solution***

For particularly tough to remove contaminants, piranha solution can be used.

#### **WARNING**

Piranha solution should be handled with extreme care; it is a strong oxidant and reacts violently with many organic materials. It also presents an explosion danger. All work should be performed under a fume hood. Wear proper protective equipment.

#### **NOTE**

There are many variations in the use of Piranha solution. The protocol listed below is provided for informational purposes only. This information is not a substitute for proper knowledge and training in handling Piranha solution.

Piranha Solution typically consists of a 30:70 v/v solution of 30% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>).

1. Heat the Piranha solution to 60° to 90° C. (NOTE: For some applications Piranha solution can also work at room temperature).
2. Place the substrates into the piranha solution for 15 to 30 minutes. The samples should begin bubbling furiously. Exact times may vary depending on the substrate used and the temperature. Prolonged exposure to piranha solution can result in sample surface roughening.
3. Remove the substrates and rinse them in a beaker filled with ultra pure water.
4. Rinse several times with ultra pure water.
5. Dry with a stream of N<sub>2</sub>.

### ***Gold Deposition***

There are three standard ways of depositing gold onto substrates: sputtering, evaporating and gold plating. Typically a thin adhesion layer of approximately 40 - 200 Å of chromium (Cr), titanium (Ti), or titanium/tungsten (Ti/W) is applied between the substrate and the gold layer. This adhesion layer helps bond the gold to the substrate and prevents peeling of the gold layer during subsequent processing and chemical treatments. If an adhesion layer is not desirable, gold can be deposited directly onto the substrate.

#### **NOTE**

**If no adhesion layer is used, the gold coated substrates should not be sonicated in future processing steps, as this will cause delamination and removal of the gold layer.**

Typical gold thicknesses are 500 to 2000 Å. A standard recipe for gold coated substrates consists of 50 Å Cr (glass substrates), Ti (glass or silicon substrates) or Ti/W (glass or silicon substrates) and 1000 Å gold (Au).

### ***Gold Purity***

Only the highest purity gold should be used for self-assembly. Impurities in the gold disrupt the gold crystal structure, which can then translate into defects in the assembled monolayer. Also, some impurities in gold can migrate to the surface resulting in an outer surface layer that is enriched in the impurity. For self-assembly, only gold with purities of 99.999% or higher should be used. Thiols will assemble on lower purity gold, but the impurities could affect the final monolayer formation and structure.

## ***Roughness***

The major effects of substrate roughness can be seen with samples used for atomic force microscopy (AFM) or scanning tunneling microscopy (STM) analysis. Since these methods both rely on placing a very fine tip in close proximity with the sample surface (either in contact or within a few angstroms) it is imperative to have substrates with atomic smoothness over areas large enough to obtain an image (for example, 100 x 100 nm). For other samples, roughness could play a role if the topography of the sample precludes the successful execution of the desired chemistry. In most cases however the sample roughness should not interfere with sample preparation due to the small dimensions of the thiols (angstroms) in comparison to the dimensions of surface topographical features (microns). The difference in scale is large enough that the thiol molecules can still coat the entire surface and produce a coating that presents the desired chemistry at the surface.

## ***Handling Gold Substrates***

Restricting the handling of gold substrates to a clean room would be ideal, but is not always possible. Nevertheless, there are steps one can take to reduce the possibility of contaminating substrates during handling. Cleaning the work area and equipment with solvents and wearing proper gloves can substantially reduce the potential for contamination. For sample handling, polyethylene gloves work best to avoid sample contamination. Natural rubber and other glove materials may contain polymer release agents that can easily be transferred to the substrate surface. If it is necessary to wear another kind of glove for personal protection, it is advisable to wear polyethylene gloves over your protective gloves to protect your samples.

Use clean forceps and tweezers to move and handle gold coated substrates. Never touch the substrates with bare hands. It takes some practice to be able to grab small silicon and glass samples without slipping and scratching the gold surface. Specialized tweezers designed for handling small thin samples are available and can be helpful.

## ***Storing Gold Substrates***

Gold is chemically nonreactive, but is instantaneously coated by adventitious hydrocarbons after exposure to the air. Minimizing exposure to the open atmosphere can reduce the potential for further contamination. To minimize atmospheric exposure, store gold coated samples in petri dishes that have been backfilled with nitrogen or argon and sealed with Parafilm. For further protection these sealed containers can be placed in a larger jar that is also backfilled with nitrogen or argon.

## **NOTE**

For straight chain alkanethiol SAMs the adventitious hydrocarbon contamination found on gold surfaces is typically not a problem. This is due to ability of the assembling alkanethiols to "scrub" these contaminants off the surface. Other thiols with large bulky head groups may not be able to fully remove the adventitious contaminants, which could result in non-ideal layer formation.

## ***Preparing Gold Substrates for Self-Assembly***

### ***Cleaning Gold Substrates***

There is some debate over whether cleaning of gold substrates is necessary. Some cleaning protocols may remove one contaminant simply to replace it with another one. Proper storage of the gold substrates reduces the need for cleaning before use for self-assembly. As mentioned above, a "clean" gold surface will always contain a layer of adsorbed hydrocarbons. In fact, when analyzed by x-ray photoelectron spectroscopy (XPS), a clean gold surface will typically show around 50% carbon, 30% gold, and 20% oxygen. Realistically, the only probable ways to avoid these adsorbed hydrocarbons are to store your samples under ultra high vacuum environments, clean your samples and transfer them into an assembly solution while still wet, or use a template stripping protocol to prepare the substrates.

It is highly recommended to carry out surface analysis on the gold that is to be used for self-assembly before beginning any experiments. We recommend using XPS since it gives a quantitative surface composition of any elements present. If only carbon, gold, and oxygen are found on the surface, it should be fine to proceed with preparing SAMs. If there are other elements present, then cleaning the gold surface, or preparing new gold surfaces would be advised.

There are several methods available for cleaning gold substrates after they have been stored. It should be noted that regardless of the cleaning protocol used, if the sample are allowed to dry and sit in air after cleaning, they will be instantly coated with a layer of hydrocarbons.

Asemblon does not endorse any particular method of cleaning.

### ***Cleaning Procedure 1:***

A simple cleaning procedure consists of rinsing the gold substrates with ethanol (to remove hydrophilic contaminants), followed by hexane (to remove hydrophobic contaminants), and finally rinsed with the solvent used during self-assembly (typically ethanol).

### ***Cleaning Procedure 2:***

An alternate method involves dipping the samples in a 0.01M hydrochloric acid (HCl) solution for 1 minute to remove hydrophilic contaminants and then rinsing with purified water, ethanol and then the self-assembly solvent (if different from ethanol).

### ***Cleaning Procedure 3:***

A more vigorous procedure involves dipping the substrates in piranha solution for a few seconds. Gold substrates should not be left too long in the solution, since gold surface roughness increases upon prolong exposure. Also, the gold layer may peel off if exposed to long to piranha solution, especially if no adhesion layer between the gold and the substrate is present.

### ***Cleaning Procedure 4:***

If the gold coated substrates have a titanium/tungsten (Ti/W) adhesion layer, the substrates can also be cleaned by passing the flame of a butane torch over the surface several times. For this a small butane torch should be used. These are typically called micro torches and produce a strong, bright blue flame. The flame tip should touch the sample and should be moved continually across the surface in a zig-zag pattern several times.

**NOTES:** This procedure only works with substrates that will not melt under the heat of the butane flame (metals, glass, silicon). The flame must not be left in one location during the cleaning as this can cause the substrates to superheat and fracture. Place the samples onto a piece of metal or ceramic so you do not burn your counter top. Do not touch the substrates directly after heating as they can be very hot. This procedure only works with gold substrates that have a titanium/tungsten (Ti/W) adhesion layer. Other adhesion layer metals will migrate through the gold and contaminate the surface. If no adhesion layer is used, the gold layer may be loosened and come off the substrate.