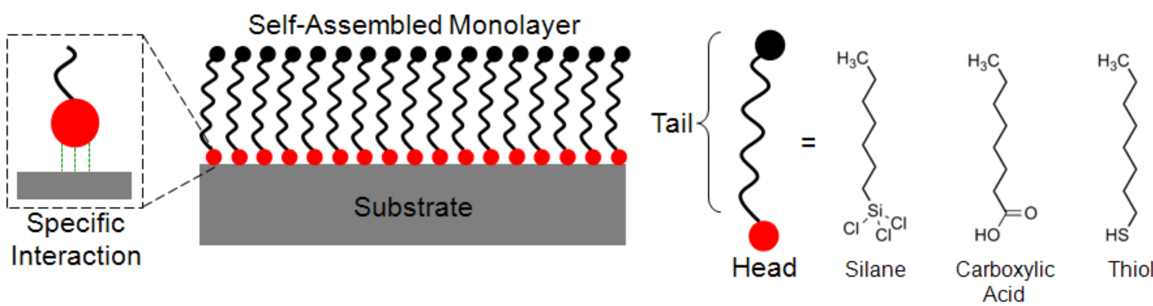
Self-Assembly Lab (50 points)

Objective: The objective of this online lab is to explore the formation of self-assembled monolayers on various surfaces and to assess the success of monolayer formation on these surfaces by measuring water droplet contact angles.

After reviewing pertinent background information the student will watch a series of videos pertaining to the bottom up nanofabrication process of self-assembly. These videos, in conjunction with background information, will provide detailed insight onto each step of the fabrication of self-assembled monolayers. After watching the videos the student will be required to answer review questions on ANGEL.

Background:

Self-Assembled Monolayers (SAMs) are organized layers of surfactant-like molecules attached to a surface. Ideally, they are only one layer thick. In this experiment, you will examine the formation of SAMs on various surfaces, including metals (Au, Al) and oxides (SiO_2). The SAMs molecules (or ligands) used in this lab will be a silane, a carboxylic acid, and a thiol. These ligands are shown in the figure below.



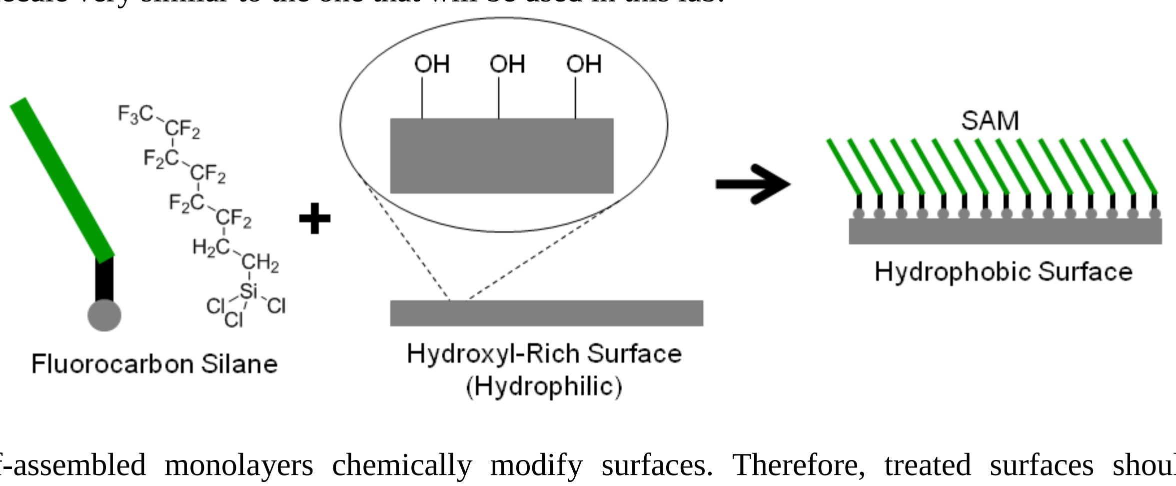
Self-assembled monolayers are used in many applications and across a variety of industries. They form extremely thin films that, depending upon the materials involved, serve many functions including: anti-fog coatings, pigment dispersal aids, mold release agents, and nanoparticle stabilizers. In the context of micro- and nano-fabrication, SAMs find uses in microcontact printing and anti-stiction coatings. SAMs are also often used to control the wettability of surfaces and to selectively protect them from harsh conditions.

The molecules that form SAMs are amphiphilic, meaning that their two ends prefer different environments. Simple surfactants, such as soaps and detergents, are commonplace examples of amphiphiles in which one end of each molecule is hydrophobic (water fearing) while the other is hydrophilic (water loving). This unique property allows detergent solutions to dissolve dirt and grease and carry them away in water – a solvent in which these hydrophobic materials ordinarily would not dissolve.

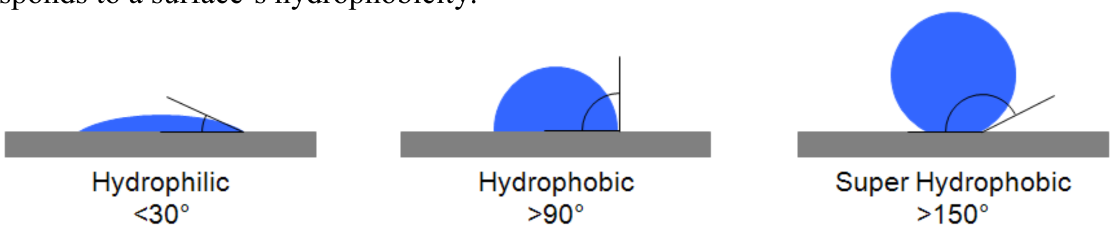
While SAM molecules (sometimes called ligands) may have hydrophilic and hydrophobic ends, the primary requirement is that they have one end that preferentially interacts with the surface of interest. As illustrated above, the head groups (red) attach to the surface while the tails (black) pack into an organized layer just above it. However, the chemical properties of the head group must complement the surface being modified. Not all amphiphilic molecules form SAMs on all surfaces. They have to be paired appropriately. Generally, ligand adsorption follows the so-called "hard-soft" rules, which relate to the polarizability of the participants (i.e., head group and surface). The more polarizable something is, the “softer” it is. Unpolarizable groups and surfaces are “hard.” Applying this concept to possible ligand choices: carboxylic acids are hard while thiols are soft. Regarding surfaces: oxides are hard and noble metals are soft. Based on these guidelines, it is possible to predict which molecules will form SAMs on a particular surface. For example, carboxylic acids (hard) should adsorb onto oxide surfaces (hard) better than thiols do. Conversely, thiols (soft) should work well when applied to gold or silver (soft). In each case, the hardness or softness of the ligand should be matched to that of the surface to be treated. However, one complicating factor not considered in this argument is whether an exposed metal surface naturally forms an oxide layer when exposed to air. A relevant example is aluminum, which quickly forms a native oxide.

The head groups of SAM molecules interact with the surface while their tails are exposed to the external environment, which may be air, water, or another solvent depending on the application. So, the chemical identity of the tail controls what properties are presented to the outside world. The simplest self-assembling molecules contain only hydrocarbon tails (hydrophobic). They could be used as water repellents, for example. However, it is increasingly common to find SAMs molecules that have more complex functionality attached to their tail ends. Ligand tails may be designed to react with, and covalently bond to, layers cast on top of the SAM. In this case, the SAM could function as an adhesion promoter. In biological applications, SAM tails may contain receptors or other molecular recognition units that are capable of bonding to specific targets or biological molecules (e.g., proteins, DNA). These are just a couple generalized examples. Since tail groups can be endlessly customized, new applications for SAMs are continuously being explored.

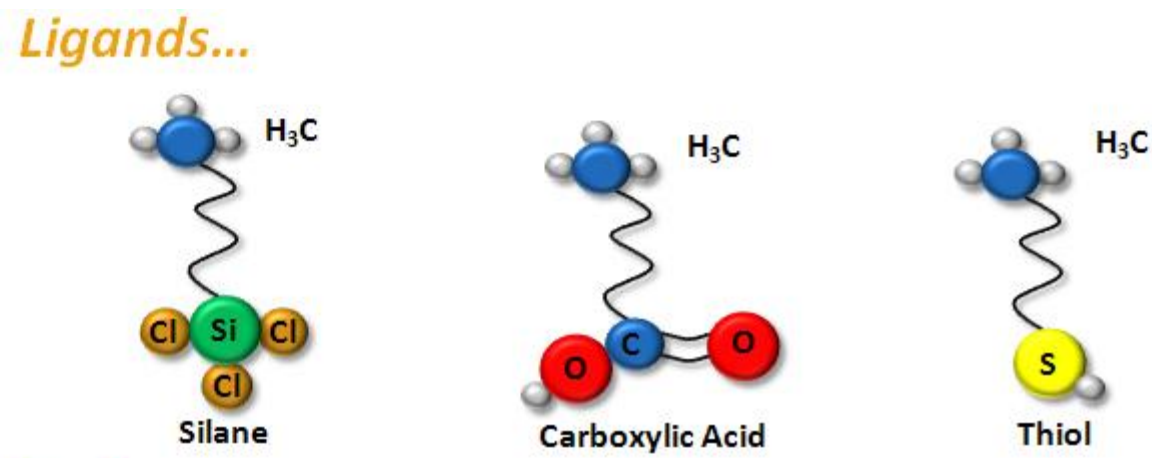
In this experiment three self-assembling materials will be fabricated: an alkanethiol, an aliphatic (hydrocarbon-based) carboxylic acid, and a trichlorosilane with a fluorocarbon tail. The surface compatibility (hard/soft rules) of thiols and carboxylic acids has been discussed above. Silanes are similar in behavior to carboxylic acids in that they bind to oxide surfaces. The trichlorosilane head group ($SiCl_3$) reacts readily with hydroxyl-rich oxide surfaces. The reaction forms covalent bonds between the silane head group and the surface. This is illustrated below for a fluorocarbon molecule very similar to the one that will be used in this lab.



Self-assembled monolayers chemically modify surfaces. Therefore, treated surfaces should behave differently than untreated ones. Since all of the SAM molecules employed in this experiment possess hydrophobic tail groups (aliphatic hydrocarbons and fluorocarbons are hydrophobic), we may be able to observe differences in the way that they interact with water before and after treatment with the various SAMs molecules. The simplest way to assess a surface's interaction with water is to measure the contact angle between the surface and a small water drop resting on top of it. The more hydrophobic a surface is, the greater the contact angle will be. This is similar to water beading up on a waxed car. On the other hand, water drops will tend to spread out on hydrophilic surfaces. Due to their increased wettability, the corresponding contact angle will be lower. The figure below illustrates how a water droplets contact angle corresponds to a surface's hydrophobicity.



The goal of this experiment is to assess which ligand molecules will form stable SAMs on the different surfaces. All of the ligands and surfaces that will be investigated are shown below:



All possible combinations of ligands and surfaces will be tested and untreated surfaces will also be assessed as a control. The main criterion for determining if a SAM has formed is whether or not the contact angle of a DI water droplet dispensed on the surface increases following treatment. An increased contact angle versus the control likely indicates a hydrophobic SAM is present on the surface.

In order to process self-assembled monolayers a set of processing conditions must be carefully followed. These steps are outlined in the videos that follow.

Step 1: Substrate Preparation

As discussed in the background section three types of surfaces will be used in this lab. A thermal evaporator can be used for creating the aluminum and gold surfaces. Feel free to review the link below for an explanation of the evaporation process.

http://www.engr.psu.edu/mediaportal/flvplayer.aspx?FileID=8e8351bc-ecb7-42ef-aff3-b

In this lab, 100 nm of Al and 100 nm of Au were evaporated onto glass slides.

To create the silicon dioxide surface an oxidation furnace can be used. Feel free to review the link below for an explanation of the thermal oxidation process.

http://www.engr.psu.edu/mediaportal/flvplayer.aspx?FileID=e7f0722a-f00c-4385-896a-9

In this lab, 200 nm of SiO_2 was grown onto a silicon wafer.

At this point, the three surfaces are ready for processing. Since 3 SAMs will be applied in this lab and a control sample is needed, each of the three samples depicted above must be cleaved into 4 separated pieces; one piece will serve as a control, one piece will be subjected to the thiol ligand, one piece will be subjected to the aliphatic (hydrocarbon-based) carboxylic acid, and the final piece will be subjected to the trichlorosilane ligand. The goal of this lab is to obtain the following matrix of data pertaining to the contact angle of a water droplet on treated and untreated surfaces:

Contact Angle (°) of a DI Water Droplet on Substrate				
Surface	Control	Thiol	Carboxylic Acid	Silane
Gold				
Aluminum				
Silicon Dioxide				

Again, an increase in the contact angle as a result of ligand treatment indicates a SAM has likely formed. Therefore, by obtaining the matrix of data above we can easily assess which combination of surface and ligand forms a SAM.

Step 2: Clean the Samples

Samples will be cleaned in preparation for ligand treatment. Watch the following video which shows how this clean is performed.

http://www.engr.psu.edu/mediaportal/flvplayer.aspx?FileID=501985a0-293d-41e3-a36f-2

Step 3: Apply the Ligands

Following the clean all samples will be subjected to the three ligands discussed hitherto. One of each type of surface (Au, Al, and SiO_2) will be subjected to each of the three ligands.

Watch the video below which shows how the TFOS (silane) ligand is applied:

http://www.engr.psu.edu/mediaportal/flvplayer.aspx?FileID=a344f139-fbe1-430c-967b-6

Watch the video below which shows how the thiol and carboxylic ligands are applied:

http://www.engr.psu.edu/mediaportal/flvplayer.aspx?FileID=457726b9-3b91-44ba-b1ab-0

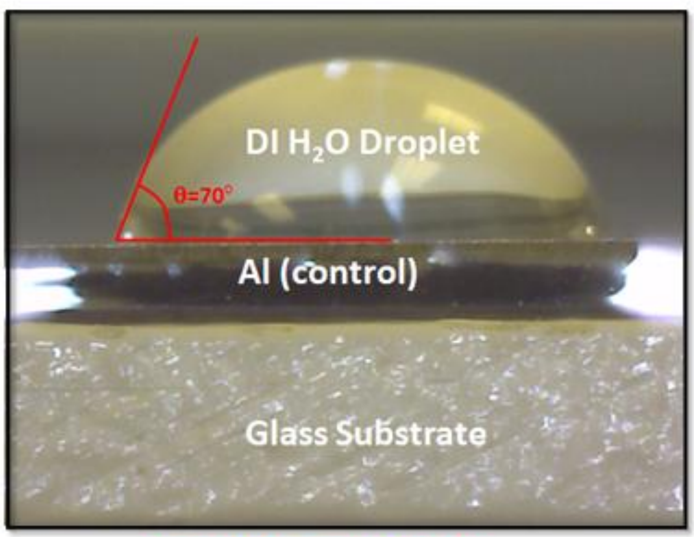
Step 4: Measure Contact Angles

Once all samples have been subjected to treatment the contact angle of a small DI water droplet on each of the 12 surfaces will be measured using a small light microscope in conjunction with an image analysis program (ImageJ). Watch this step at the link below:

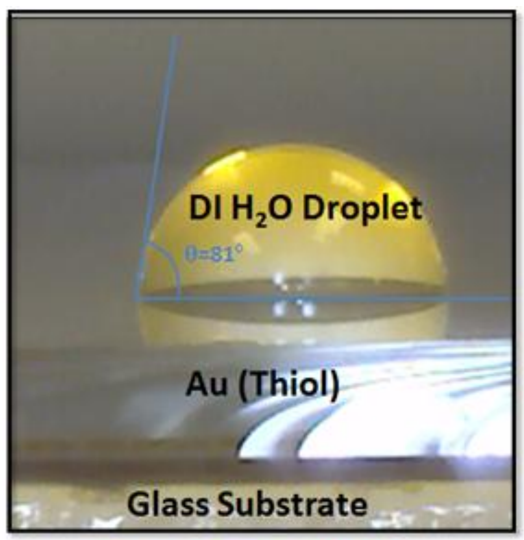
http://www.engr.psu.edu/mediaportal/flvplayer.aspx?FileID=55dbba52-e0da-4c46-ac5d-6

Step 5: Analyze the Data

The following images show additional data that was obtained during this experiment. Here, the case of the control Al sample and the case of the thiol treated Au sample are shown. In all, 12 images must be obtained in this fashion. Obtaining the contact angle measurement for each image will allow the matrix of data introduced in step 1 to be completed.



Control Al Sample: θ=70°



Thiol Au Sample: θ=81°

After obtaining all 12 contact angle measurements the data in the following data resulted. The two example measurements depicted above are color coded for clarity within the table. The contact angle that was measured in the previous video is also shown in green (Al surface with silane treatment).

Contact Angle (°) of a DI Water Droplet on Substrate				
Surface	**Control**	**Thiol**	**Carboxylic Acid**	**Silane**
Gold	72	81	71	68
Aluminum	70	73	78	63
Silicon Dioxide	56	49	52	83

The data in this table should be used when answering questions 11 through 14. Questions 15 and 16 require you to apply the concepts in this lab to additional scenarios.

Questions to be answered on ANGEL (NO HARD COPY REQUIRED)

1. Which is the following is not an application of a SAM? (3)
2. What is an amphiphilic molecule? (3)
3. Select the true statement pertaining to the polarizability of surfaces and SAMs: (4)
4. What cleaning process was used to prepare the substrates for treatment? (3)
5. What were the parameters for the dehydration bake? (2)
6. How much TFOS (silane) was dispensed into the glass vial for the silane treatment? (2)
7. Which of the following ligands were applied with a solution based technique? (3)
8. How long were each of the 3 ligand treatments conducted for? (3)
9. Why is a micropipette used to dispense the DI water droplet? (3)
10. What characterization tool was used to image the DI water droplet? (3)
11. Based on the data obtained in this lab (second table) which ligand formed the most successful SAM on the gold surface? (3)
12. Based on the data obtained in this lab (second table) which ligand formed the most successful SAM on the aluminum surface? (3)
13. Based on the data obtained in this lab (second table) which ligand formed the most successful SAM on the gold surface? (3)
14. Based on the data obtained in this lab (second table) which surface appears to be naturally the most hydrophilic? (4)
15. Based on the results from this lab, which type of ligand might you use to form a SAM on a copper coated substrate (hint: copper oxidizes)? (4)
16. How would the water contact angle of gold change if it was treated with a thiol containing a hydroxyl group (water loving) at the end of its tail? (4)