Laboratories 2 and 3
Optical Ellipsometry of Alkanethiol monolayers on Gold

OBJECTIVE: To measure the thickness and structural evolution properties of alkanethiol monolayers on gold substrates.

Need 3 substrates per group

1. Monolayer formed from 10^{-4} M $C_{18}H_{37}SH$ in *n*-hexane using piranha-cleaned substrate
2. Monolayer formed from 10^{-4} M $C_{18}H_{37}SH$ in *n*-hexane using plasma cleaned substrate
3. Monolayer formed from 10^{-4} M $C_{18}H_{37}SH$ in *n*-hexane using freshly evaporated gold substrate (TA evaporates substrates, students watch).

Lab 2.

Step 1. Make alkanethiol solution.

Step 2. Clean all glassware with piranha solution and rinse with solvent. Use 3 different substrates as indicated above for monolayer synthesis.

Step 3. Measure the ellipsometric response of the clean substrates to obtain optical constants (n and k).

Step 4. Prepare monolayers.

Step 5. Measure the ellipsometric thickness of each sample right after it is made.

Step 6. Store the samples in cleaned sample bottles containing 10^{-4} M thiol/hexane solution.

Lab 3.

Step 7. Measure ellipsometric thickness of each sample 1 week after formation. Keep this sample for use in contact angle measurements later in the lab period.

Step 8. Immerse one monolayer in clean *n*-hexane and let it soak for one week. At the beginning of the next lab period (Lab 4), remove the substrate from the solvent, dry it and measure its thickness.

Step 9. Start the contact angle measurement experiment.

Laboratories 2 and 3

Measuring the Thickness of a Molecular Monolayer

While there are a variety of optical methods that have been developed over the past 50 years to measure the concentrations of molecules or infer information on their structure and/or conformation, most of that work has been performed in solution or in the gas phase. It has become increasingly clear, however, that a dominant trend in molecular sciences of all sorts is the study and utilization of interfaces and surfaces. Two obvious examples are biological membranes that serve to mediate many complex biochemical functions, and chromatographic separation media, that are used to execute separations of complex and often similar molecules.

The study of surfaces and interfaces is often limited by the small amount of material present at the actual interface, and under certain conditions it is difficult to separate the response of molecules adsorbed at a surface from those present in the bulk medium near the surface. These constraints are particularly true for optical measurements of surface properties. In this course, we will examine the utility and limitations of two optical methods used widely for the characterization of monolayers of molecules adsorbed on surfaces. For these systems, there are essentially three questions that can be addressed by such measurements.

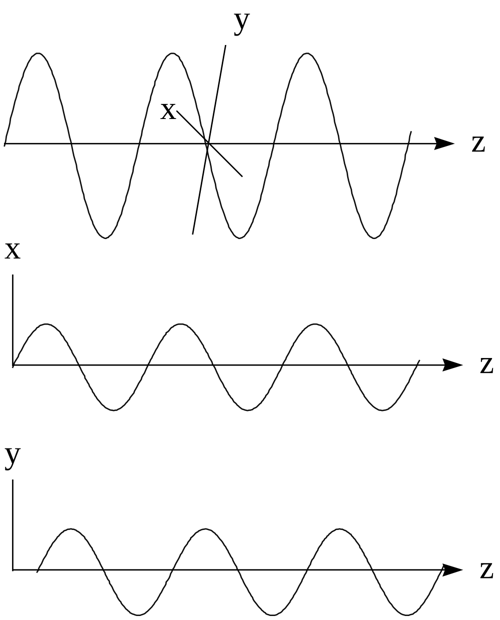
1. How much of the monolayer is present?
2. How organized or random are the constituent molecules within the monolayer?
3. What is the average orientation of the monolayer? (Do the molecules lay parallel to the surface, normal to the surface or something in between?)

In two experiments you will perform this semester, we will address these questions through two measurements.

1. Measurement of the thickness of the monolayer.
2. Measurement of the IR absorbance of the monolayer.

For the present experiment using ellipsometry, we discuss below how to measure the thickness of thin films of material, where both the real and imaginary part of the complex dielectric response of the material must be considered.

Optical ellipsometry. The fundamental principle behind optical ellipsometry is that the properties of an electromagnetic wave will be altered by its reflection from a surface. The polarization condition of any electromagnetic field can be deduced from its Cartesian components.



In other words, the polarization condition of an arbitrary sinusoidal oscillation can be given by:

$$E = E_x + E_y = E_0 \sin(\omega t - \phi)$$

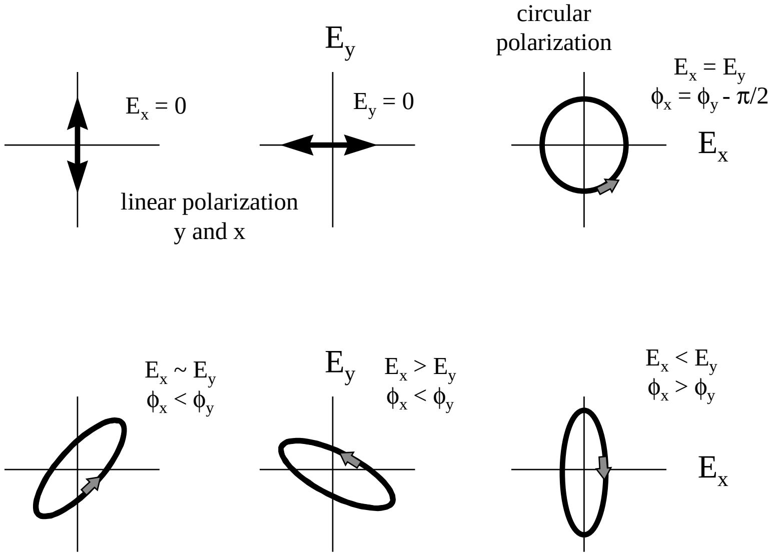
$$E_x = E_0^x \sin(\omega t - \phi_x)$$

$$E_y = E_0^y \sin(\omega t - \phi_y)$$

Where the magnitudes of E_0^x and E_0^y and the phase terms ϕ_x and ϕ_y are used to describe the polarization condition of the electromagnetic field E.

The polarization condition of the light can be described conveniently by plotting the relative values of E_x and E_y through a single cycle of ω from 0 to 2π. The resulting vector describes the polarization condition and directionality of the light. It is important to keep in mind that, in general, light is elliptically polarized, and that both linear and circular polarization conditions are limiting or special cases of elliptical polarization.

Based on the Fresnel equations and intuition, it is apparent that the polarization condition of a light beam will be changed by its reflection from a surface. In general, both the relative phase angle and the relative amplitude of the Cartesian components of the light can be altered by the reflection process. These changes in polarization condition resulting from reflection can be used to determine the complex dielectric response and thickness of any film(s) or overlayers on the reflective surface. We have discussed the Fresnel equations in class and their application to optical ellipsometry.



Experimental Procedures

For the ellipsometric measurement it is first necessary to measure the real and imaginary parts of the refractive index of the cleaned blank substrates. In doing this it is necessary to adjust the angle and height of the sample stage to ensure accurate measurement.

Carefully place the substrate on the sample stage and start the WVASE program. Go to the hardware pull down menu and select *initialize*. During initialization, software looks for the instrument configuration, the rotating analyzer is brought up to speed and data acquisition is synchronized with the rotating analyzer. Next, in the hardware menu, select *align*. The ellipsometer contains a 4-quadrant detector. To insure that the sample is flat, the signal to each of the quadrants should be identical. Adjust the tilt of the sample stage so that the red cross is in the center of the cross-hairs on the screen. This alignment step can be completed only under the condition that the sample is flat. Now go to the hardware menu and select *calibrate*. This calibration is necessary to determine the exact positions of the input and analyzer polarizers and the relative attenuation of the ac signal relative to the DC signal. (See the short course on ellipsometry for details and an explanation of the specific parameters.)
You are now ready to measure the optical constants for each substrate.

General Information:

Solutions: For all of the substrates you will use, the monolayers will be formed from a 10^{-4} M solution of 1-octadecanethiol ($C_{18}H_{37}SH$). A total volume of 250 mL will be sufficient for your experiments.

Substrates: You will require three substrates for this experiment. For each case, a 1 cm x 1 cm substrate is fine and will be provided to you by your TA. Of the three substrates, you will need to clean one using piranha solution, clean one using the plasma cleaner, and one will be prepared directly by the evaporation of gold. You should react this substrate with alkanethiol solution immediately after its preparation and measurement of optical constants.

Glassware: You will need three 125 mL Erlenmeyer flasks, one 250 mL volumetric flask, and one 10 mL pipette for the solution work. Piranha solution is 3:1 sulfuric acid:hydrogen peroxide (100mL is plenty). **For the piranha solution, make sure to follow the safety precautions indicated in Laboratory 1. Wear a lab coat or apron, a full face shield and rubber gloves**.

Exposure of the substrates to all solutions is carried out by clamping the crystals with a plastic hemostat and suspending them in solution for the period of time indicated. Thirty seconds in fresh piranha solution should be sufficient to achieve proper cleaning. Exposure to the alkanethiol for approximately 30 minutes is appropriate for the initial formation of the monolayer on all substrates. For the substrate prepared by evaporating gold, it should be immersed in the alkanethiol solution after making ellipsometric measurements. By allowing the monolayer to form over a longer time period, a high quality monolayer should result.

Procedure for Laboratory 2

1. Initialize and calibrate the ellipsometer as described in Laboratory 1. (You do not need to recalibrate the angle of incidence. Use the angle that you measured last time.)

2. Set up your "model" on the ellipsometer. You are going to start with simply a gold film as the model. (The gold film is sufficiently thick and absorptive that the light will never reach the underlying adhesion layer or the silica.) Go to the model window. Select <u>adlayer</u> and add the film au.mat. Choose to fit *n* and *k* by checking the appropriate boxes. Do not fit the thickness. Make sure that the selected thickness of the gold is in the mm range. This will insure that the model doesn't try any reflections from the back side of the gold. The ellipsometer is now ready and waiting for your gold samples.

3. Go with the TA to the evaporator and watch the evaporation of Cr and then Au on the glass substrate.

4. Determine the *n* and *k* values for the evaporated substrate. The specifics are as follows. Go to the hardware window. Select the <u>ellipsometric data</u> pull down menu and click on <u>acquire single scan</u>. This measures the Ψ and Δ values over the full wavelength range. Next go to the <u>fit</u> window. Click on <u>normal fit</u>. This will fit *n* and *k* values for the gold film to the Ψ and Δ values at each wavelength. To see the results, go to the <u>model</u> window. Click on the gold layer. Click on <u>optical constants</u> to see the data. While there, save the data file so that you will have it for future measurements. Note the values of *n* and *k* at 633 nm. They should be around 0.1-0.2 (*n*) and 3.4 (*k*). Take a quick look at the graph window. Note that the fit of the data to Ψ and Δ is perfect. You measured two things at each wavelength and you used two parameters, *n* and *k*, at each wavelength to fit the data.

5. Immerse the slide in the thiol solution. It will be in the solution for 30 minutes.

6. Prepare a fresh piranha solution. As described above, immerse one of the gold-coated slides in the piranha solution for thirty seconds. Rinse the slide copiously with deionized water and dry with nitrogen.

7. Measure the optical constants of the piranha-cleaned slide and save them for future measurements. Immerse this slide in a thiol solution. It will be in the solution for 30 minutes.

8. Clean a gold slide with the plasma cleaner. To do this, first turn on the vacuum pump and fill the dewar for the trap with liquid nitrogen. This will insure that oil from the pump does not backstream into the plasma cleaner. Put your sample in the plasma cleaner. Open the valve to the vacuum pump while installing the face cover of the plasma cleaner. Let the vacuum run for about 2 minutes. Next open the needle valve to the plasma cleaner so that the Ar pressure to the plasma cleaner is about 0.2 Torr. Turn the plasma cleaner to low power. You will now see the purple or orange color due to the ions in the plasma. Leave the substrate in the plasma for 2 minutes. Turn off the plasma cleaner and close the valve to the vacuum

pump. Open the needle valve and the face cover of the plasma cleaner will become loose in a few seconds. Remove your sample and measure its ellipsometric constants as described above. Save these constants. Note the constants at 633 nm and then immerse the sample in a thiol solution.

9. After a sample has been immersed in thiol solution for 30 minutes, remove it and rinse copiously with hexane and distilled water. Dry the sample with nitrogen. Now measure the film thickness. To do this, go to the model window. Click on add layer and select generic film. This is a file with a generic refractive index of 1.5 and an absorption coefficient of zero. (Look at the optical constants to verify this.) Select the approximate thickness of this film as 20 Å and choose to fit the thickness. Do not fit the optical constants as this film is too thin for effective fitting of constants (your homework will show you why). Make sure that the bottom layer corresponds to the optical constants that you measured for this sample. Do not fit the optical constants of the substrate. (You already measured those.) Make sure the *n* and *k* boxes on the substrate are not checked. Finally go to the hardware window and click ellipsometric data and acquire single scan. Go to the fit window and select normal fit. Record the thickness. Do the measurement and fitting three times to get a feel for the precision of the measurement. Look at the graph window. Is the fit still good? Now you are fitting Ψ and Δ at 44 wavelengths (88 measurements) to one parameter. Do you think that the fit is good? Try one other thing. Use the substrate parameters measured for the other two samples in the model. How is the fit now and what thickness do you get?

10. Repeat the ellipsometry measurements for the other two films.

11. Immerse all of the samples in the thiol solutions for next time.

12. Take a moment to grasp this. You just measured a film that is one molecule thick. With this ambient instrument you measured a thickness to a precision of 10^{-8} cm. This is rather remarkable when you think about it.

Questions on the Experiments

1. In your measurements, you likely found that the measured thickness of the monolayer varied as a function of the substrate on which it was prepared. Offer an explanation for this finding that is consistent with the literature.

2. An ellipsometer uses light that has a wavelength of ~ 6330 Å, yet it is sensitive to the presence of films on a surface that is ~ 10 Å thick? Why?

3. Ellipsometry is a unique surface science tool because it can measure the thickness of very thin films in an ambient background (room air). Often adventitious contamination from the surrounding environment can produce tens of Å of contamination on a surface. What accounts for the unique ability of the ellipsometer to perform “surface science” measurements in room air?