

Student Activity

Microcontact Printing on Gold CD-Rs

Developed by: Michael Davis, Harold Washington College

Graduate Student Mentor: Mohammad Parpia

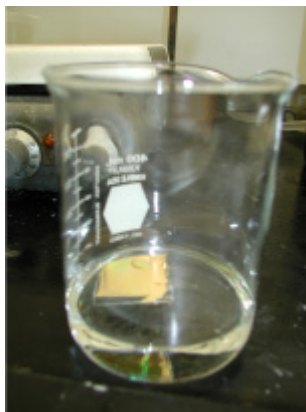
Faculty Advisor: Joseph Hupp

Preparation of the Gold Substrate (do this activity individually)

1. Using scissors cut a piece of the Gold CD-R to an appropriate size.



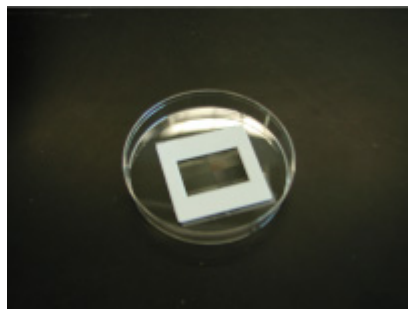
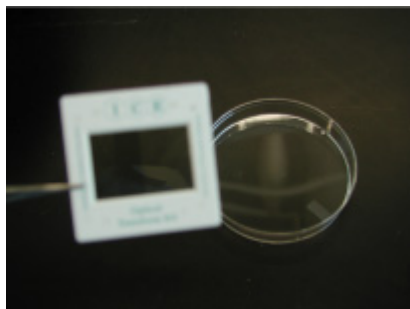
2. Drop the CD-R into a concentrated HNO_3 solution and let it sit for about five minutes. A thin film should be seen floating away from the CD-R.



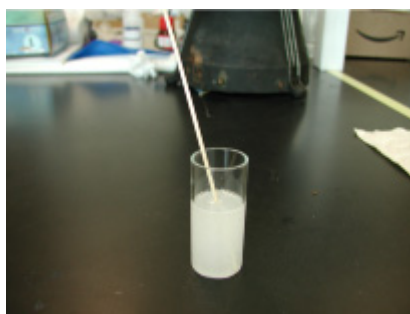
3. Remove the gold CD-R with tweezers and rinse it with ethanol. Dry the substrate under nitrogen or allow the ethanol to evaporate at room temperature.

Preparation of the PDMS Stamp:

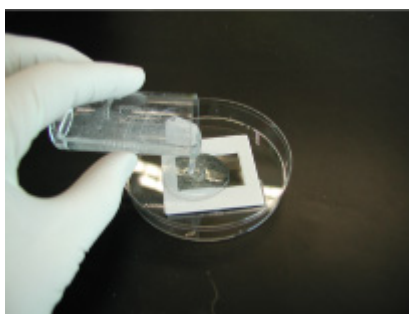
1. Affix an ICE optical transform slide (labeled side down) to the bottom of a petri dish with some glue or epoxy.



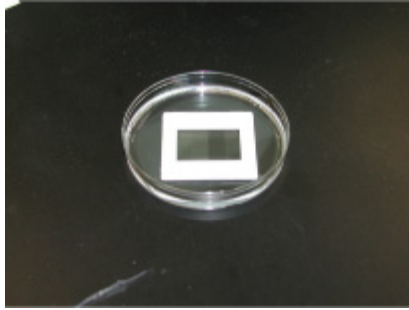
2. In a separate vial, beaker, or cup, mix roughly 12 g of the PDMS elastomer with 1.2 g of the elastomer curing agent (10:1 ratio). The solution will be very viscous. Stir the solution vigorously and let it stand for about 30 minutes. Most of the large bubbles should rise to the top in that time.



3. Slowly pour the solution over the top of the slide. Pour in the center, and the liquid will run to the outside.



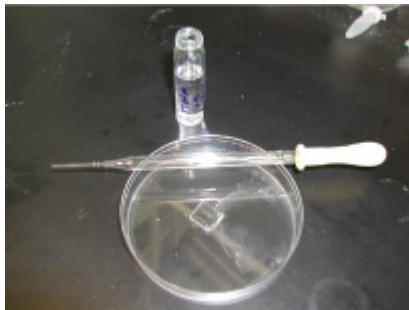
4. Let stand for about 1-2 hours or until all of the small bubbles have popped. The liquid should look clear.



5. Put the petri dish in an oven at 65 °C for about 2 hours to cure the polymer.
6. After removing the petri dish from the oven, use a razor blade to cut away the patterned portion of the stamp. Be careful not to touch the patterned portion of the stamp.

Inking the PDMS Stamp:

1. Prepare a 2 mM solution of mercaptohexadecanoic acid (MHA) in ethanol.
2. Apply drops of the MHA solution to coat the entire surface of the stamp. Let the stamp sit for several minutes.

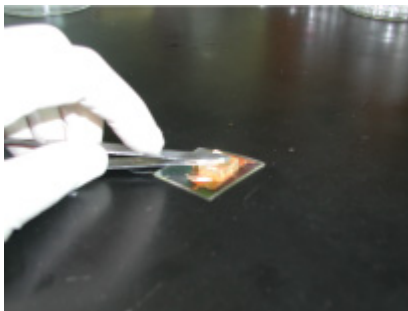


3. Rinse the stamp with excess ethanol, and dry it under nitrogen.

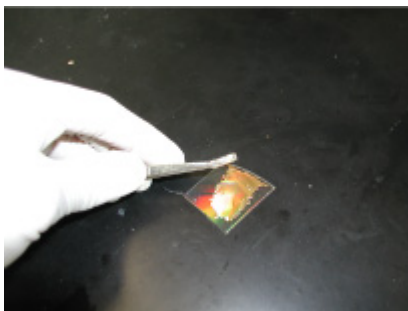


Patterning the Gold Substrate:

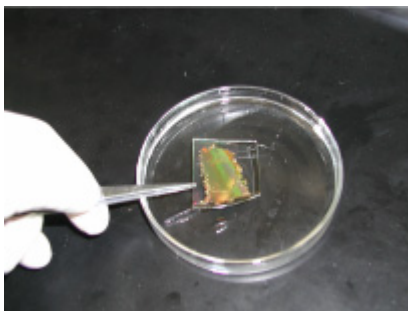
1. Place the patterned, inked side of the stamp down on the surface of the gold substrate for about 10 seconds with light pressure.



2. After 10 seconds, carefully remove the stamp. Set the stamp aside.



3. Immerse the stamped gold substrate in a 2 mM solution of octadecanethiol (ODT) in ethanol. Let the CD-R sit for about five minutes.

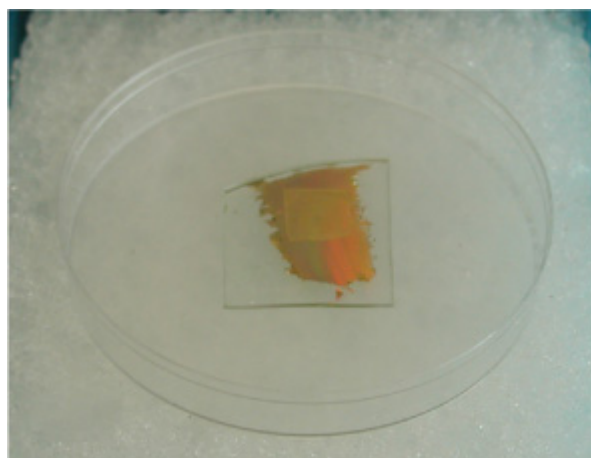


4. Carefully remove the substrate and rinse with ethanol. Blow it dry with nitrogen.



Revealing the patterned surface:

1. To make the pattern appear, place the substrate in a petri dish, gold side up, and place the dish over ice. A pattern should be immediately observable.



2. To quickly observe the pattern simply breath on the substrate. Moisture from the breath is enough to reveal the pattern.

HAZARD: *Concentrated nitric acid is a strong acid and a strong oxidizing agent. It is destructive to skin and to eyes. Extreme care must be taken when working with concentrated nitric acid.*

HAZARD: *Ethanol is a flammable solvent. Care should be taken in storing and handling ethanol. Mercaptohexadecanoic acid (MHA) may be an irritant to the eyes, the respiratory system and the skin. Thiols have an unpleasant odor, however ODT and MHA are both solids at room temperature and are non-volatile enough to be used without a fume hood.*

Questions: (To be answered on a separate piece of paper.)

1. Microcontact printing represents one type of lithographic technique. What are some other techniques that could either transfer or create a pattern on a suitable substrate? (It will be necessary to look up additional sources for this. Please cite these sources.)
2. What amino acid(s) could be isolated with this technique? Would the modified surface be hydrophilic or hydrophobic? Explain why.
3. Why is the gold substrate stamped before it is immersed in the other alkanethiol? Explain what the consequences might be.
4. What is Moore's Law? Describe how this lab activity could be tied to Moore's Law. (Please be specific.)

Instructor Information

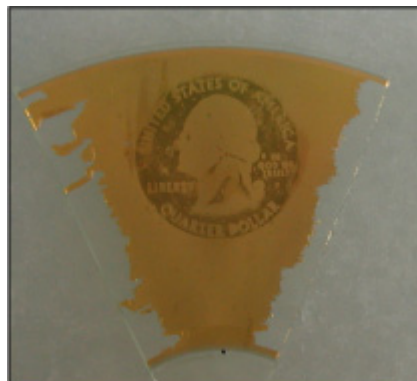
Microcontact Printing on Gold CD-Rs

Developed by: Michael Davis, Harold Washington College

Graduate Student Mentor: Mohammad Parpia

Faculty Advisor: Joseph Hupp

Objective: To functionalize a gold surface with hydrophilic and hydrophobic regions using microcontact printing.



Techniques:

- Microcontact Printing
- Self-Assembly

Materials Needed:

- | | |
|--|---------------------|
| • Concentrated nitric acid (HNO ₃) | • Beaker |
| • Ethanol | • Tweezers or tongs |
| • 16-Mercaptohexadecanoic Acid (MHA) | • Gloves |
| • Octadecanethiol (ODT) | • Gold CD-R |
| • Ice | • Scissors |

Introduction:

Nanotechnology is the application of the size and shape dependent properties of particles that have one dimension that is smaller than 100 nm. A nanometer is 100 millionths of a millimeter. It would seem very difficult to create, let alone build with, something that small. Yet it happens.

The project was developed as part of the Research Experience for Teachers (RET) program at the Northwestern University Nanoscale Science & Engineering Center. Funding for this program is primarily provided by the Nanoscale Science and Engineering Initiative of the National Science Foundation under NSF Award Number EEC-0118025.

In this size regime, the bulk properties of matter that we take for granted, like density, boiling point, and even color, change dramatically. This represents a relatively new field for scientists to explore. Using newly developed nanotechnology, quantum properties of matter can be observed and bulk physical and chemical properties can be predicted.

As scientists look for ways to miniaturize our current technologies to make them faster, smarter, and less expensive, they frequently turn to the nanometer size regime. In this kind of synthesis, two things are of the utmost importance:

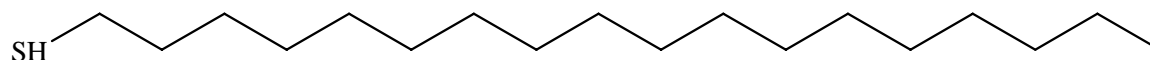
1. Particles that are all the same shape and size (monodisperse).
2. Ability to arrange these particles in some predetermined way (self - assembly).

This lab will focus on the second of those goals.

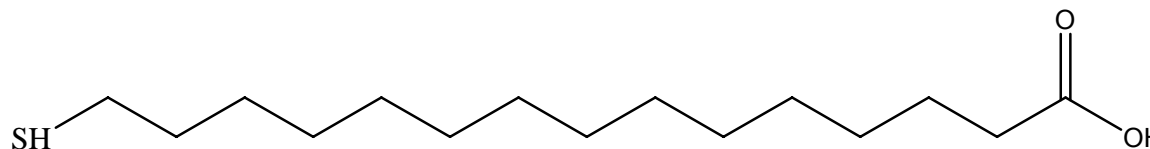
Self-assembly is remarkable technique that can be used in the creation of large structures. It is akin to something 'building itself'. Imagine being able to build a castle out of Legos, just by drawing a picture of the castle, and dumping the Legos over it. This would save us the time and energy it would take to handle each individual Lego.

From a molecular point of view, self-assembly represents the ability to create a molecular structure by carefully manipulating the physical and chemical properties of the reagents being used. This lab will make use of gold, alkanethiols, and water.

Thiol groups (-SH) have a strong affinity for gold, and form strong covalent bonds (Au-S) with gold films. The thiols being used are below, octadecanethiol (ODT) and 16-mercaptohexanoic acid (MHA).



Octadecanethiol



16 - Mercaptohexadecanoic Acid

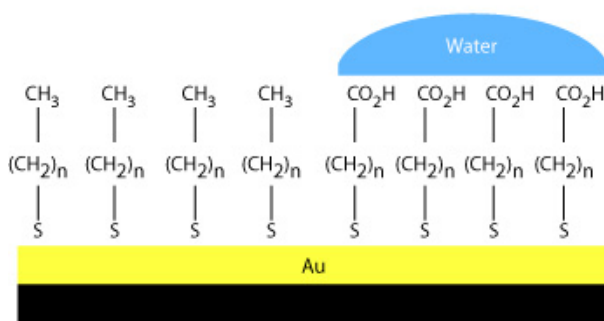
Both of these molecules have a thiol group, but they have different functional groups on the their opposite terminus. ODT has a methyl group on its terminus and is therefore hydrophobic while MHA has a carboxylic acid group making it hydrophilic.

These molecules will be arranged on the gold surface through microcontact printing (μ -cp). This technique utilizes an elastomeric stamp, much like a rubber stamp that teachers might have used to adorn exceptional papers with smiley faces. This stamp, once created will be inked with one of the two molecules above, and then pressed against a gold surface. The

The project was developed as part of the Research Experience for Teachers (RET) program at the Northwestern University Nanoscale Science & Engineering Center. Funding for this program is primarily provided by the Nanoscale Science and Engineering Initiative of the National Science Foundation under NSF Award Number EEC-0118025.

thiol on the stamp will covalently bond with the gold substrate. After the stamp is removed, the substrate will be immersed in the other thiol, forming more covalent bonds. At this point the surface will be covered with alkanethiols that are hydrophilic or hydrophobic in a specific pattern.

To see the distinction between the two, we will cool the substrate down so that water will condense on it. A pattern will become visible as the water assembles onto the hydrophilic pattern. The hydrophobic portion does not get wet (see figure below).



Answers to Questions

1. Microcontact printing represents one type of lithographic technique. What are some other techniques that could either transfer or create a pattern on a suitable substrate? (It will be necessary to look up additional sources for this. Please cite these sources.)

This question is a chance for students to explore the world of nanostructure design. It would be advisable to establish a preferred list of sources, so that students are not doing a random Google search. One general method would involve deposition or controlled growth through some kind of mask. Whitesides article in *Small* 2005 (1, No.2, 172-179) is a good information source.

2. What amino acid(s) could be isolated with this technique? Would the modified surface be hydrophilic or hydrophobic? Explain why.

The amino acid that could be easily isolated is cysteine, which has a thiol side chain. The amino acid contains polar groups, which can be readily ionized thus making the surface hydrophobic.

3. Why is the gold substrate stamped before it is immersed in the other alkanethiol? Explain what the consequences might be.

Immersing the bare gold substrate in an alkanethiol will completely cover the surface with that molecule. The surface, already being modified, could not be further altered through a stamping process. It would be completely covered with one molecule, and there would be no differentiation.

4. What is Moore's Law? Describe how this lab activity could be tied to Moore's Law. (Please be specific.)

Unless this subject is specifically addressed in the context of the lab, students will most likely do a random Google search for the information. Moore's Law is a general observation about the number of transistors that can be fit onto an integrated circuit, since its invention. Every year, twice as many transistors have fit into the same amount of space, which means that the size of the transistors has shrunk tremendously over the past forty years. Lately this has been interpreted to include data memory. Over the past 40 years, techniques like microcontact printing have been employed to make smaller transistors, and put them closer together. This lab is an exposure to a technique that endeavors to put two distinct things very close together without bringing them into contact.