Characterization of Mercury and Copper Capped DMBP Monolayers

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Abstract and Introduction:

One bottom-up nanotechnology approach is self-assembly. Molecular self-assembly is a process by which atoms, molecules or groups of molecules arrange themselves spontaneously into regular patterns without outside interventions. Phenyl thiols are aromatic compounds that easily react with gold (Au), and have an electron flow through the π-system.

We formed a monolayer of 4,4'-dimercaptobiphenyl dithiol (DMBP) on an Au <111> substrate via self-assembly. We characterized the monolayer by ellipsometry and utilizing two surface probe microscopy (SPM) techniques including atomic force microscopy (AFM) and scanning tunneling microscopy (STM).

The DMBP monolayers were further reacted with solutions of either copper $(Cu)^{+2}$ or mercury $(Hg)^{+2}$ via an oxidation-reduction reaction resulting in either DMBP-Cu^{+1} or DMBP-Hg^{+1} to form a metal-capped monolayer. We examined the capped monolayers with SPM, and we also prepared a nanograft of DMBP in decanethiol in preparation for STM experiments. The expectation was that electrons in DMBP would flow through the π-systems of phenyl groups, the d orbitals of the terminating sulfur, and finally through the d orbitals of either Cu or Hg.

Objectives:

Our goals included; characterizing the monolayer surface using ellipsometry and SPM, determine if the redox behavior of Cu- and Hg- capped DMBP will affect the resistance of the monolayer using a probe station experiment of patterned substrates, and STM measurements of the n-decanethiol nanografted monolayer.

Experimental Procedure:

All glassware was cleaned with piranha solution. The Au substrates were cleaned by hydrogen flame annealing. This method also provided large grain terraces of Au. We heated the quartz and then swept back and forth on the Au substrate at a frequency of 1 Hz for 30 to 60 seconds, while keeping the flame tip at a 30° angle with respect to the Au surface.

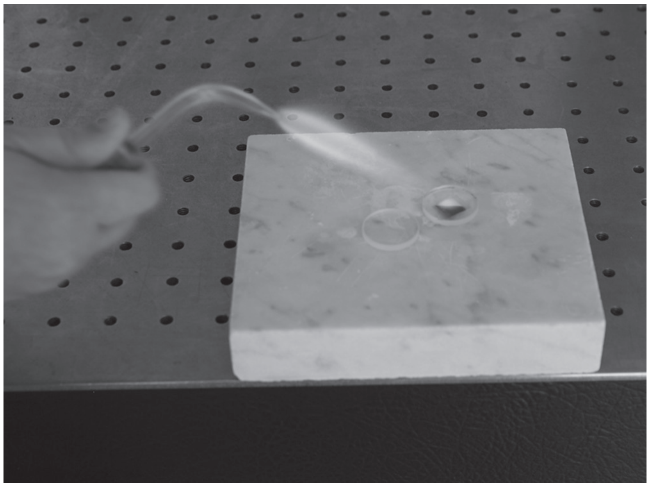

Figure 1: Hydrogen flame annealing.

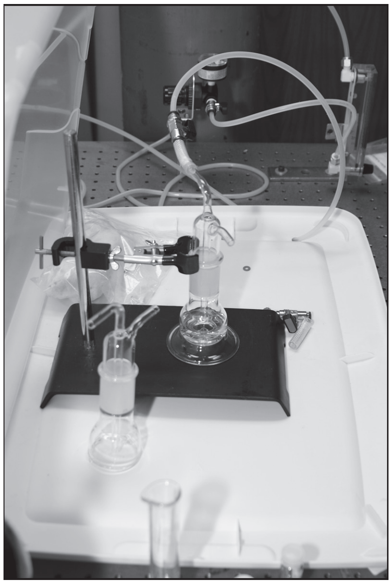

Figure 2: Monolayer apparatus.

With this procedure, we observed the desired small flame spot and dim orange colour on the Au substrate. In Figure 1, we see that this method assisted in cleaning the Au substrate. After flame annealing, the optical constants of the Au <111> were obtained by ellipsometry. A monolayer of DMBP was prepared via self-assembly by submerging a clean Au <111> substrate in a 1 μm solution of DMBP under nitrogen (Figure 2). After forming a monolayer of DMBP, a two hour reaction, we obtained the optical constants associated with the monolayer.

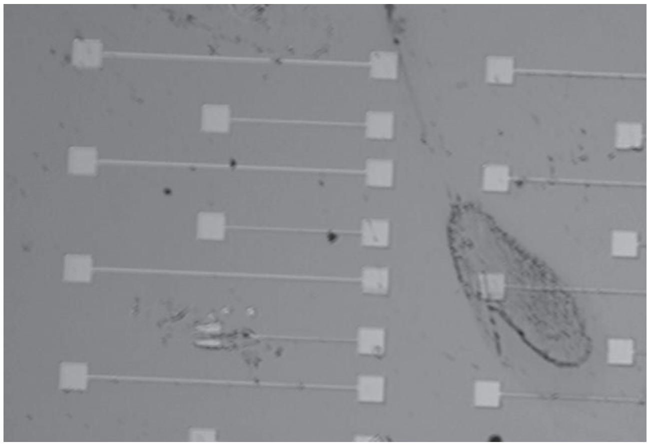

Figure 3: Photoresist pattern created by photolithography.

Given the optical constants and published refractive index, we were able to use a computational model to obtain the thickness of the monolayer. This procedure was repeated for three different areas on each substrate, and we reported the average thickness. Also, we created a photoresist pattern (Figure 3) by photolithography for the probe station experiment.

A nanografting technique was used to prepare samples for STM measurements. To nanograft, we zoomed into a 2 μm × 2 μm area, which was relatively flat with a very small force. Then, we increased the force on the AFM probe and swept three times. Finally, we returned to low force, zoomed out and imaged the shaved area. If a hole was created by nanografting, it was back-filled with the molecule to be investigated, because the small area of molecule was an ideal to measure the resistance behavior.

Results:

The average thickness of the monolayer samples was 0.9 nm. We compared our results with the 1.06 nm thickness obtained by ChemDraw 3D. The average thickness of the monolayer measured by ellipsometry was consistent with the thickness of DMBP that was associated a 19° tilt with the surface normal, thus accounting for the difference in height between the model height of DMBP and the height measured by ellipsometry. Further the measurement was consistent with previous data of DMBP monolayer.

AFM and STM confirmed the surface order and provided a visual picture of local features. We compared the length of grain terraces of Au <111> with and without flame annealing. Figure 4 shows that Au <111> with flame annealing produces larger grain terraces. Also, the image of Au <111> with flame annealing shows contamination. This contamination could be caused by not cleaning the quartz properly or by the condensation produced by the hydrogen flame. Later monolayers were prepared on fresh Au <111> samples which were stored under nitrogen. Unfortunately, the STM was not working properly, and for this reason we could not complete the part of nanografting.

Future Work:

Run the probe station experiment and STM measurements of n-decanethiol nanografted monolayers to determine if there is a difference in resistance between Cu^{+1} and Hg^{+1} capped DMBP monolayer.

Conclusion:

We prepared DMBP and DMBP Cu- and Hg- capped monolayers on Au <111> substrates. The average thickness of the monolayer measured by ellipsometry was consistent with the thickness of DMBP monolayer associated with a 19° tilt angle with respect to the surface normal, as reported in previous experiments.

Also, we characterized Au <111>, flame annealed Au <111>, and monolayers of DMBP, and Cu and Hg capped DMBP surfaces using contact mode AFM, contact mode AFM in liquid, and STM. By these methods we observed that flame annealing produces larger grain terraces of gold. We also discovered contamination from flame annealing. We used contact mode AFM for nanografting DMBP in a decanethiol matrix.

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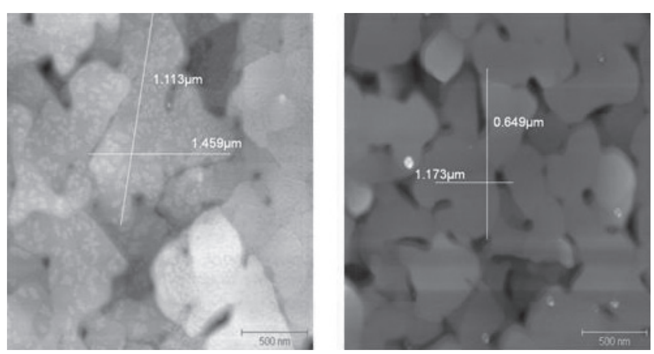

Figure 4: Hydrogen flame annealed Au <111> and non flame annealed Au <111>.