Patterning Soft Materials with Light-on-Tip

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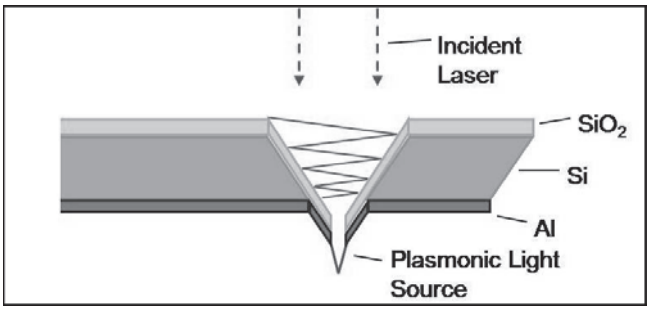

Figure 1: Cross section of the plasmonic scanning probe.

Abstract and Introduction:

The objective of this project is to stimulate cell membrane proteins, through a nanofabricated plasmonic scanning probe tip mounted in near-field scanning optical microscopy. Near-field scanning optical microscopy is a method that allows for sub-wavelength resolution optical imaging and collection along with spectral and topographical information. This is made possible by using light emitted in the near field from a sub-wavelength aperture on a scanning probe tip. Since the far field resolvable spot size is limited due to the Abbe diffraction limit [1], our probe utilizes surface plasmon resonance [2] to emit light from the aperture. Since these fields are attenuated, this effect can only be utilized within the decay range. Our group has attained aperture sizes as small as 66 nm. Figure 1 shows a cross-section of the plasmonic probe, with surface Plasmon resonance occurring at the aluminum-silicon dioxide interface.

For this Research Experience for Undergraduates Program, calibration of the plasmonic enhanced scanning probe tip was performed by measuring the dependence of exposure depth on exposure time in photoresist spun onto a glass substrate. Models were constructed using COMSOL finite element method for comparison. To prepare to stimulate proteins using the plasmonic tip, we also demonstrated a microcontact printing technique to pattern protein on glass substrate using a polydimethylsiloxane stamp. Using the near-field light source from our probe to locally stimulate cell proteins will allow us to examine gene expression with high precision.

Experimental Procedure:

The major focus of this summer research program was calibration and simulation of the plasmonic probe, as well as the demonstration of a protein sample preparation method. Demonstration of a method to prepare protein monolayer samples is important to test the probe's ability to isolate proteins for stimulation before it is used on living cells. To prepare the monolayers, we employed a microcontact printing technique. Rabbit Immunoglobulin G-Fluorescein isothiocyanate conjugated protein was micropipetted onto a hydrophobic polydimethylsiloxane (PDMS) stamp, rinsed in phosphate buffered saline and then deionized water, air dried, and depressed onto either a glass or porous silica substrate. Figure 2 depicts the stamped protein monolayer in a 20 μm diameter circle pattern and scanning electron microscope closeup.

To calibrate our probe and evaluate the plasmonic effect, a near-field photolithography experiment was performed. A 1.4 μm layer of AZ-5209 E positive photoresist was spun onto a glass substrate and mounted in our near-field scanning optical microscopy setup. A plasmonic probe with a 500 nm aperture diameter fed with 405 nm light was used to expose photoresist point by point with exposure times varied between 0-8 minutes. The resulting exposure pattern was developed and evaluated using atomic force microscopy.

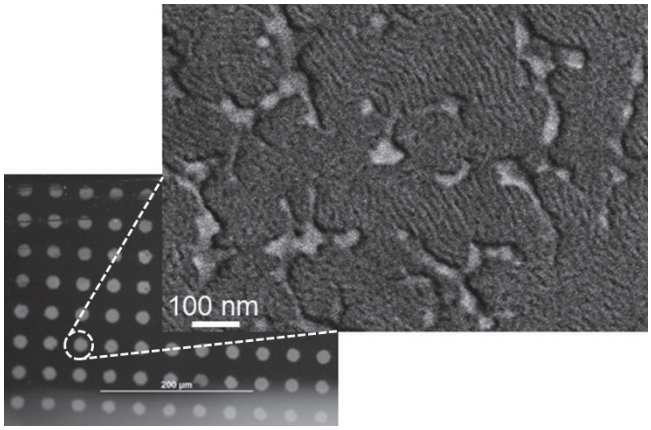

Figure 2: Optical and scanning electron microscope image of stamped protein monolayers.

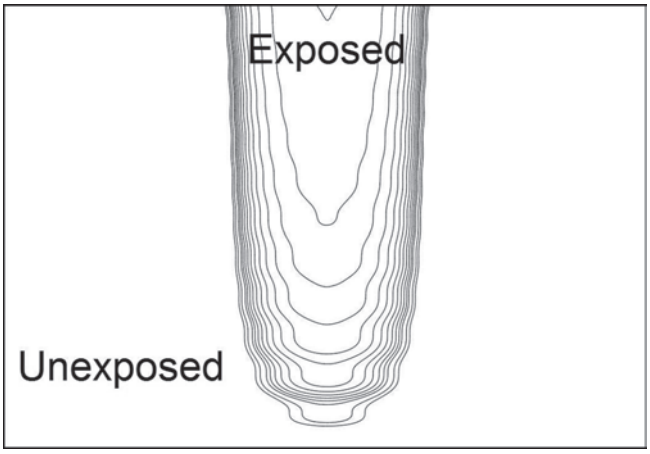

Figure 3: Simulated exposure contours for unexposed photoresist.

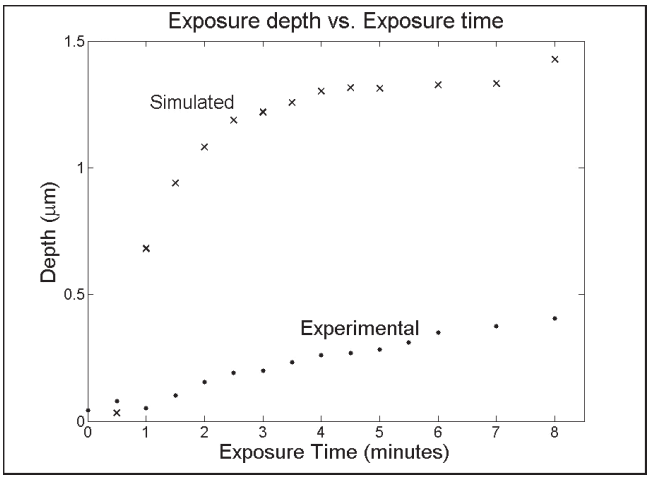

Figure 4: Exposure Depth vs. Exposure Time for near-field photolithography experiment.

Comsol finite element method software was utilized to simulate the near-field photolithography experiment. The photoresist layer was modeled two dimensionally as a rectangle with a height of 1.381 μm and a 500 nm-full width half maximum Gaussian source opposed at the center of the upper side. The power of the light source was calibrated to a value on the same order of magnitude as the first experimental value, which was 6.5 microwatts. To simulate the light transmission within the photoresist, iterated steady-state solutions were performed for each time step. Using the clearing dose parameter for AZ-5209 E photoresist, we calculated the minimum power flow required to expose the photoresist for each time step. The exposure contours calculated for completely unexposed photoresist are shown in Figure 3. A "cone" of exposed photoresist with the same depth and radius as the previous time step's contour was defined using two second-degree Bezier curves for each iteration to approximate the index change from exposed to unexposed photoresist. The resulting depth values were recorded and compared to the experimental values.

Results and Conclusions:

Simulated and experimental exposure time-depth relationships are shown in Figure 4. For the first depth value, simulated and experimental results are comparable. This is to be expected, as it is the calibration point. We have determined several possible sources for the disparity in the rest of the depth values. Contact of the plasmonic tip with the photoresist, the inability of the optical simulation to account for the development process, and limited probing depth of the atomic force microscope tip are some possible sources of error. We can conclude that one of the significant source of error is the inability of the simulation to account for near-field waves with a transmitted Gaussian source. If the source included the decaying component, the simulated values for the first few depths would be higher, allowing for a lower power value in the simulation, which would in turn bring the rest of the data points down closer to the experimental data. We therefore conclude that the plasmonic effect occurred during the near-field photolithography experiment.

Future experiments involve photosynthetic reaction center membrane proteins from *Rhodobacter sphaeroides* bacteria [3], where these proteins will be arranged in a monolayer where each isolated proteins or protein groups will be stimulated with high spatial-temporal resolution with subsequent photosynthetic current measured.

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