My summer project consisted of a plan to use a modified version of micro-molding in capillary (MIMIC) patterning to locally de-functionalize Graphite Oxide films. This would allow for selective patterning of conducting and insulating regions on chemically modified graphene sheets, as a more ecologically friendly material than ITO. There are several methods of producing the films, but scalability remains an issue for using graphene-based materials in practical products. The MIMIC-based method I proposed was ambitious, as the professors who I consulted with about the project told me, but that it was worth attempting.

The general process used was to prepare PDMS stamps, as PDMS is one of the common materials used for soft lithography patterning techniques. PDMS happens to be unresponsive to the chemicals that were to be used. Graphite Oxide films were prepared with two distinct methods. A Langmuir-Blodgett approach was used to create single-atomic layer and few atomic layer GO samples, while drop-casting was used for macroscopic films of GO. Drop-casting was preferred, as even a reduced single layer of of GO is not conducting enough for many purposes. Drop cast films were thick enough to be visible, but thin enough to be transparent.

The stamps were pressed onto the GO films on glass and silicon oxide substrate and the sample was introduced to a Hydrazine vapor environment (very roughly 0.7 g/L) with elevated temperatures, the sample was removed after a set period of time in the reducing environment. The sample was then rinsed in deionized water, dried at 50 degrees Celsius for 1 to 2 hours.

Many reiterations of these steps were taken, with variation of N_2H_4 concentration, stamp pressure, temperature, time. However, one critical problem plagued the experiment from start to finish. Areas reduced were marked by a visible change from GO's characteristic brown to a transparent graphitic gray. However, a persistent problem throughout: the resolution of the pattern was poor to nonexistant. Adjusting temperature, stamp compression, and time treated, among other parameters, would not show much improvement, bleeding effect would be larger than 1 millimeter in typical treatments. The poor resolution is clearly not acceptable for practical applications or processes. This unforseen diffusion problem can to a small extent be mitigated by treatment in short cycles of about 5 minutes of Hydrazine vapor, with breaks in between of 15 minutes or longer. However, the problem is not diminished to the point of practical use, with bleeding effects still on the scale of millimeters, and this processing plan does not meet the goals for micropatterned GO/reduced GO films that the project set out to accomplish. The fast rate of diffusion of Hydrazine at this scale seeps through the sealed areas under the PDMS stamps and reduces them as well. Under higher pressures (stamps clamped to substrate), the bleeding is slowed, but no patterns appear whatsoever in the unreduced regions. This leads me to believe that using MIMIC to pattern hydrazine-reduced regions of GO is not feasible through this route without significant tuning of physical parameters, beyond the scope of a summer project.

However, after useful discussion with group members, at the twilight of the summer, a new direction for the project was decided. Since the problem was with diffusion, a slower-moving reducing agent was chosen: ascorbic acid. This may diminish the reduction level achieved, but the benefit of being patternable would outweigh the cost. In addition, to further improve patternability, Polyvinylpyrrolidone was discussed as an addition to the reducing solution as a means to increase viscosity and reduce bleeding. Samples were done with values of 1:16 up to 1:1 PVP:ascorbic acid solution, by volume. The pH levels of the solutions ranged from 3 to 3.5, the higher pH's belonging to higher concentrations of PVP. The ascorbic acid was in the concentration found in literature for GO reduction, at 5g/L. PDMS stamps were firmly pressed against the film and it's substrate. The solution was placed at the edge of the top stamp, with a 5 to 10 degree slope, ensuring that the capillary

channels were lined up for the drop to drain through. The drop was allowed to run for a set time (five minutes to one hour), and then placed onto a hot plate at 70OC for 60 minutes.

Although the characterization steps for these samples has not started yet, results show more promise than the hydrazine method did. Optical microscopy shows patterns that may possibly be patterned areas of reduction, based on contrast levels. Further testing will be performed, including AFM (atomic force microscopy), to determine if it is just contaminant layers. If not, then LFM (lateral force microscopy), FTIR (Fourier Transform Infra-Red) Spectroscopy, and FQM (Fluorescence Quenching Microscopy) may be performed to determine the level of reduction that has occurred.

Figure 1: Mimic-based patterning on GO film with Ascorbic Acid treatment using a 20 micron channel size stamp.

In conclusion, this summer's ambitious goal was not met as I had hoped. However, a new spin-off project has been formed from it, which may yet yield the desired results for chemically patterned GO/ r-GO films using simple, scalable soft lithography techniques. The experience of setbacks has also taught me many personal lessons about how to better conduct research, which is also important for the educational aspect of the undergraduate summer research program. So although the research did not yield the results lofty results that were hoped, it still was in many ways a successful and productive summer, with work that will continue into the academic year. The project will hopeful expand, and has been a valuable learning experience as well.

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