

METHOD FOR PATTERNING POLY(ACRYLIC ACID) SACRIFICIAL  
LAYERS FOR USE IN SOLDER-BASED  
SELF-ASSEMBLY

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## ABSTRACT

Solder-based self-assembly is a method for micromachining three-dimensional structures on silicon. This process has been used for educational purposes due to the significant experience gained by students interested in semiconductor processing. However, patterning the silicon dioxide sacrificial layer, involves handling hazardous materials such as buffered hydrofluoric acid. To provide a safer alternative to this dangerous etchant, we describe a method for using poly(acrylic acid), a water soluble polymer, as a patternable sacrificial layer in the solder-based self-assembly process.

Key to this method, in order of steps; is the use of thermal crosslinking, a partial development technique; oxygen plasma ashing; and a strong alkaline solution to etch the sacrificial layer and reflow the solder. Plasma ashing is important to keep water and alkaline developers from etching the vulnerable poly(acrylic acid) layer too early in the process. This method is able to achieve the goal of promoting the self-assembly of three-dimensional structures on silicon. Beyond its use in our solder-based self-assembly process, this method may also prove useful in any application requiring the use of a patternable sacrificial layer made from poly(acrylic acid), as well as other polymers of a similar nature.

One such application is explored, in which the technique for patterning poly(acrylic acid) is used as a potential way to pattern crystal colloidal masks of nanospheres for use in nanosphere lithography. This technique allows for spin-coating, an inexpensive deposition technique, to be used to both form and pattern these nanosphere masks with micro-scale features.

## DEDICATION

This thesis is dedicated to those professors, colleagues, fellow students, family members, and friends who helped to support and guide me on this, the start of my journey, into the world of academia. I hope that I have made, and will continue to make, all of these people proud as I move forward with my life and career.

## LIST OF ABBREVIATIONS & SYMBOLS

PAA	Poly(acrylic acid)
SBSA	Solder-based self-assembly
HF	Hydrofluoric acid
DI Water	Deionized water
CCM	Crystal colloidal mask
HCP	Hexagonal close-packing/packed

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## CONTENTS

ABSTRACT.....	ii
DEDICATION.....	iii
LIST OF ABBREVIATIONS & SYMBOLS.....	iv
ACKNOWLEDGEMENTS.....	v
LIST OF TABLES.....	vii
LIST OF FIGURES.....	viii
INTRODUCTION.....	1
I. PREVIOUS RESEARCH.....	4
II. EXPERIMENTAL.....	6
A. Thermal Crosslinking of PAA.....	7
B. Partial Development During PAA Photolithography Step.....	8
C. PAA Window Etch Using Oxygen Plasma Ashing.....	9
D. PAA Removal and Reflow Via Aqueous NaOH Solution.....	9
E. PAA SBSA Process Description.....	10
III. RESULTS AND DISCUSSION.....	14
IV. FURTHER APPLICATIONS.....	22
V. SUMMARY AND CONCLUSIONS.....	27
REFERENCES.....	29
APPENDIX A. Copper Plating Bath Set-Up Instructions.....	31
APPENDIX B. Copper Plating Bath Operation Instructions.....	36

## LIST OF TABLES

1. The fraction of successfully folded structures and the resulting folding rates for each type of polyhedra present in the sample used for Figure 8 and Figure 9 .....	21
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## LIST OF FIGURES

1. The SBSA process flow using SiO <sub>2</sub> as the sacrificial layer .....	5
2. The PAA SBSA process flow .....	7
3. Photograph showing a degraded PAA film exposed to temperatures above 200°C .....	15
4. Optical micrograph of an overdeveloped and undercut square feature .....	16
5. Optical micrograph of a square feature after having been etched via an oxygen plasma asher .....	17
6. Optical micrographs showing square window features after a complete oxygen plasma ashing etch step and resist strip .....	18
7. Optical micrographs showing incomplete PAA removal after the completion of oxygen plasma ashing and resist strip .....	19
8. SEM micrographs of successfully folded 3D polyhedra below their corresponding 2D flat patterns .....	20
9. SEM micrographs of some notable failures .....	20
10. Process flow for crystal-colloidal mask embedded in PAA patterning process .....	23
11. Optical micrographs of some preliminary successes of the process flow seen in Figure 10 .....	25
12. Full set-up for custom copper plating bath in laboratory used for SBSA process .....	35

## INTRODUCTION

The use of three-dimensional (3D) structures is present in many areas of micro-engineering, including MEMS, photonics, and micro-electronics.<sup>1-6</sup> When fabricating these 3D structures, various micromachining techniques are used, such as micro-stereolithography, LIGA, self-assembly, etc.<sup>7-12</sup> In the work of Rao et al.<sup>13-17</sup> a process of performing solder-based self-assembly (SBSA) was developed. In work inspired by earlier researchers,<sup>18-22</sup> a method by which reflowing solder initiates folding of flat 2D patterns into 3D structures is explained and analyzed. However, in Rao's method, an integral aspect of this process involves a sacrificial layer of silicon dioxide ( $\text{SiO}_2$ ) beneath the sides of 2D copper flat patterns. The latter steps in the process flow require removing the  $\text{SiO}_2$  layer, thus leaving the copper faces that were built upon the  $\text{SiO}_2$  to be free-floating and, upon reflow of the solder covering them, initiating folding of the structure sides upwards and forming the 3D structure. These structures take the form of various polyhedra, including truncated pyramids, square boxes, and octagonal prisms, to give a few examples. There is a hazard associated with this sacrificial layer however, as it is etched using hydrofluoric acid (HF) which is an extremely toxic chemical.

One option for replacing  $\text{SiO}_2$  as a sacrificial layer in the SBSA process is the use of water-soluble polymers, such as poly(acrylic acid) (PAA). This polymer has been investigated in micro-engineering by various groups,<sup>23-25</sup> and its potential as a sacrificial layer and patternable material has been explored previously in the work of Linder et al<sup>26</sup> and other groups.<sup>27, 28</sup> Unfortunately, the presence of water in the original SBSA process, in particular during the

development stages of the various photolithography steps where water is not only used for rinsing but is also present in the developer itself, makes direct replacement of PAA for SiO<sub>2</sub> as the sacrificial layer impossible. During those steps in which water is used, the PAA sacrificial layer is prematurely etched, thus removing its effectiveness as a support structure. Furthermore, the PAA is sensitive to alkaline solutions, so the developer also acts as an etchant for the layer.

To rectify this issue, it was found that the PAA layer could be crosslinked to make it more resistant against etching by water. Afterward, a partial development, such that a thin layer of resist is left on top of the PAA, to protect it from the alkaline developer. Next, an oxygen plasma asher could be used to cut through the remaining resist, as well as the PAA, in order to pattern the sacrificial layer. This method resulted in windows through the PAA to the wafer that had clean, sharp edges as desired. Unfortunately, during the final steps of the SBSA process, when the PAA sacrificial layer needs to be removed, the layer was crosslinked even further by exposure to heat making the etching process difficult, and resulted in a need for a new way to etch said x-PAA layer. Through the review of work done by various groups, it was found that crosslinked PAA is still susceptible to being dissolved in solutions held at higher pH levels, such as aqueous solutions of sodium hydroxide (NaOH).<sup>29, 30</sup>

With this in mind, the final removal of the PAA sacrificial layer is accomplished using a solution of NaOH, which is further capable of initiating the eventual folding to form the polyhedra due to the heat of mixing when forming the solution of NaOH. Stemming from these changes in the original SBSA process, this work presents a new and modified version of the SBSA process in which the SiO<sub>2</sub> sacrificial layer is replaced by PAA. This PAA SBSA process, as it will be called, should serve as a safer and more user-friendly form of the original SBSA process and, thus, be a more attractive method for forming 3D structures on silicon. This is

especially true when used in educational settings, or also useful if an application requires patterning PAA.

## I. PREVIOUS RESEARCH

Figure 1 shows the SBSA process flow developed by our group. This process provides a method by which 3D polyhedra can be formed on a silicon substrate via the use of traditional photolithographic techniques to make 2D flat patterns. Note the polyhedra base will be formed inside the window created in the  $\text{SiO}_2$ , or sacrificial layer. The polyhedra faces will be placed on top of the sacrificial layer. This approach allows the base of the structure to remain anchored to silicon when folding occurs. Copper is used to fill the patterns. Once formed, these copper faces are covered with a low melting point solder and subsequently reflowed in hydrochloric acid heated to  $60^\circ\text{C}$ . Upon reflow, the surface energy is favorable for solder pulling the faces of the 2D flat patterns out of the silicon plane, resulting in their coming together to form various 3D polyhedra, depending on the design of the original flat patterns. Our work on developing the PAA SBSA process stems from a desire to make this process more accessible to students being trained in semiconductor processing by removing the need for HF acid to etch the  $\text{SiO}_2$  sacrificial layer. This is done by replacing the  $\text{SiO}_2$  layer with the water-soluble polymer PAA which, even when crosslinked, can be etched using a relatively safe alkaline solution.

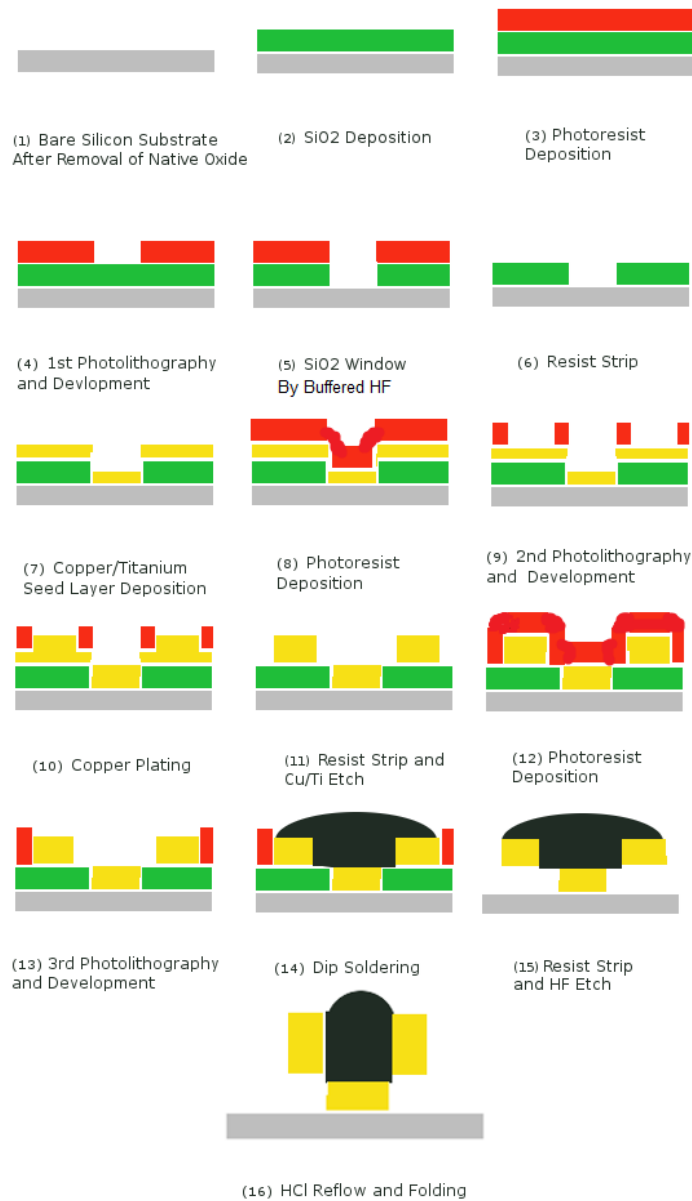


Figure 1. The SBSA process flow using SiO<sub>2</sub> as the sacrificial layer. Each step of the process is labelled below the graphic illustrating that step in a cross-sectional format.

## II. EXPERIMENTAL

Figure 2 shows the process flow for our PAA SBSA method that utilizes PAA as a sacrificial layer. As compared to the SBSA method outlined in Figure 1, there are four main challenges that had to be addressed in order to accommodate the use of PAA as a sacrificial layer: (1) the use of thermal crosslinking to reduce the solubility of the PAA in water; (2) the use of a partial development technique in the first photolithography step to avoid premature etching of the PAA layer due to water and the alkaline developer; (3) the use of oxygen plasma ashing to etch through the partially developed photoresist and PAA windows; and (4) the use of an aqueous NaOH solution to both remove the PAA sacrificial layer and cause the solder to reflow in the final steps. Each of these four areas will be explored in more detail below, followed by a full description of the PAA SBSA process.

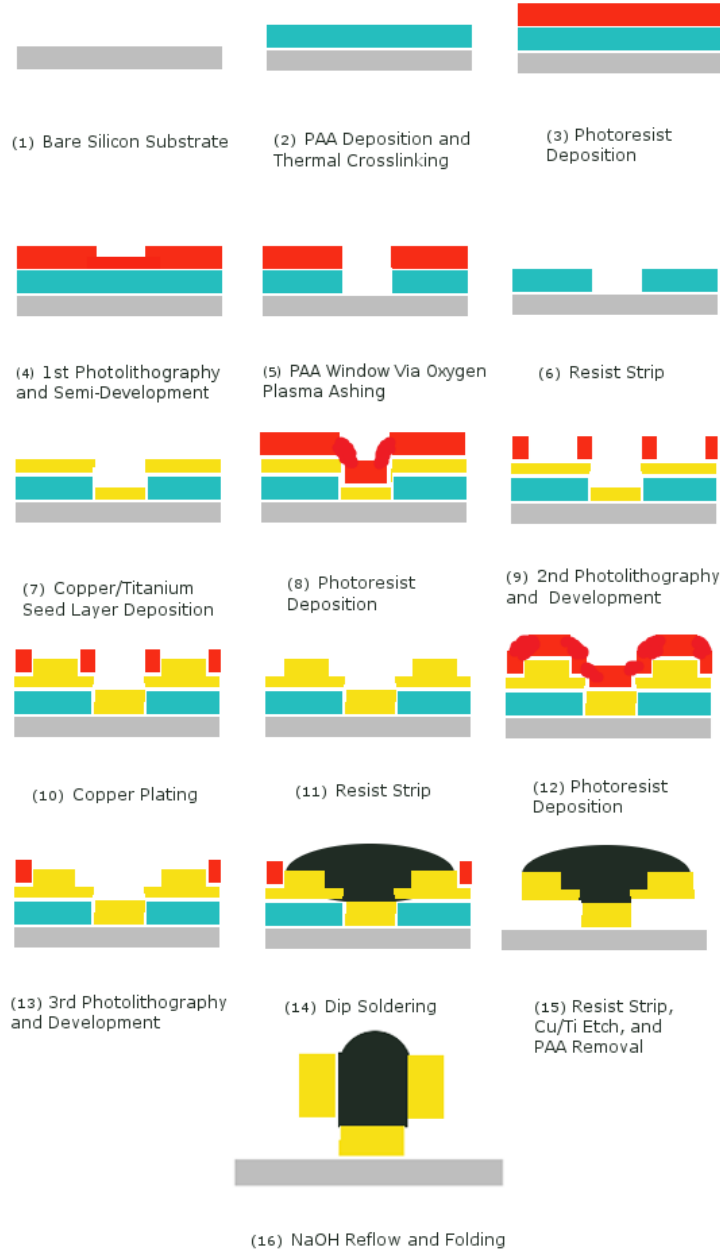


Figure 2. The PAA SBSA process flow. Each step of the process is labelled below the graphic illustrating that step in a cross-sectional format.

### A. Thermal Crosslinking of PAA

Step 2 in Figure 1 illustrates the thermal crosslinking of the PAA sacrificial layer.

Crosslinking, was performed in a Lindberg Blue M oven set to 200°C. The wafer was placed in



the furnace on the bottom side of a glass petri dish for support. The wafer was heated for approximately two hours at this temperature. To test for polymer crosslinking, the edge of the wafer was dipped into a shallow dish of deionized (DI) water. Any etching of the PAA layer, as a result of the exposure to water, would indicate the need for further heating at the same temperature in the furnace.

The addition of this thermal crosslinking step ensures that the PAA layer is durable and able to withstand the minor exposures to water, as well as the stress that it undergoes, in subsequent process steps.

#### B. Partial Development During PAA Photolithography Step

Step 4 in Figure 1 illustrates the partial development of the photoresist layer used in the first photolithography step. As in a typical photolithography step, the resist layer is exposed for the recommended time, which is six seconds for Shipley S-1818 photoresist. Following the exposure, the wafer is then placed in a petri dish filled with enough Microposit MF-319 developer solution to cover the entire sample. Normally, the duration of this development step is 60 seconds with some agitation, followed by rinsing in water and drying with a nitrogen gun. In our partial development procedure, the photoresist layer is developed for approximately 35 seconds with no agitation and immersed in deionized water for only a few seconds. After this, the wafer is then dried using a nitrogen gun, with the areas where the features are present given special attention.

This step ensures that the PAA layer underneath the photoresist is protected from any etching by both the alkaline developer solution, as well as the water used to rinse the wafer.

After performing this step, the areas of exposed photoresist should be thinner than the unexposed portions, but not completely removed.

### C. PAA Window Etch Using Oxygen Plasma Ashing

Step 5 in Figure 1 illustrates the use of oxygen plasma ashing to perform the window etch in the PAA sacrificial layer. To perform this step, a YES Plasma Asher was used. The partially developed samples were placed on a rack inside the plasma asher and an oxygen plasma ashing step was performed for multiple nine minute intervals. Time intervals were necessary due to equipment limitations. After each ashing session, the samples were monitored under an optical microscope to see whether the partially developed resist layers, and the PAA layer underneath them, had been completely etched away. Ashing continued until this was the case, usually requiring times as long as 40 - 60 minutes depending on the sample.

The addition of this step allowed for the partially developed, and thus thinner, layers of photoresist to be completely removed before the unexposed, and much thicker, photoresist. In turn, the remaining unexposed resist acted as a physical mask for the PAA sacrificial layer beneath it and thus allowed the PAA layer to be patterned with the desired windows. Upon stripping the photoresist, the quality of the patterned windows is monitored and confirmed using an optical microscope.

### D. PAA Removal and Reflow Via Aqueous NaOH Solution

Steps 15 and 16 in Figure 1 show the removal of the PAA sacrificial layer and the reflow of the solder that results in the formation of the final 3D structures. In performing this step, a 3:1 volume solution of DI water to NaOH (about a 0.1 M NaOH solution) was placed in a beaker.

Upon mixing this solution to ensure that all of the NaOH was dissolved, the exothermic nature of the dissolution causes the mixture's temperature to rise to about 80°C. Once this happens, the sample is immersed into the solution using tweezers and agitated by hand until the PAA film pulls away. After this has occurred, the sample is removed from the solution, and rinsed with water to remove any remaining PAA. Finally, the rinsed sample is placed back into the NaOH solution and agitated by hand. At this time, the solder present on the 2D flat patterns begins to reflow and, as a result, 3D structures are formed on the sample. These can be observed under an optical microscope. Naturally, over time the temperature cools and the solution is no longer suitable for reflow—but external heating would remedy this problem.

This step ensures that the crosslinked PAA sacrificial layer is able to be removed from the sample. The removal of this PAA layer allows for the faces of the 2D flat patterns to freely float and, thus, fold upwards when solder reflow occurs. The reflowing is largely caused by the heat produced by the alkaline NaOH solution and, similar to the use of hydrochloric acid in the original SBSA method, initiates the eventual folding to form the 3D structures.

#### E. PAA SBSA Process Description

The PAA SBSA process begins by cleaning a 4-inch diameter silicon wafer. In a cleanroom environment, larger particulates are removed from the wafer using a nitrogen gun. Afterward, the wafer undergoes an organic clean on a Solitec spin coater by applying acetone for 10 seconds, a combination of acetone and isopropanol for 5 seconds, and only isopropanol for 5 seconds, all at 300 rpm, and then finally spun dry for 30 seconds at 2500 rpm. After this basic cleaning, the wafer is ready for further processing.

Next, a 6 mL solution of 5 wt% PAA in water is prepared in a small beaker. A bottle of 25 wt% PAA in water from Alfa Aesar was used and, thus, water was added to reduce its weight percent. Ideally, this solution is prepared several hours ahead of time in order to minimize the presence of bubbles in the solution, which would otherwise affect the quality of the applied film during spin coating. Once this solution is prepared, it is applied onto the center of the wafer with a syringe and immediately put under a spin coating regimen of 5 seconds at 300 rpm to spread and 30 seconds at 3000 rpm to reach its final thickness of roughly 200 nm. After spin coating, the wafer is baked on a 115°C hotplate for 10 minutes in order to further remove excess water from the film. After this bake, the wafer is then placed inside a furnace and brought up to a temperature of 200°C for 2 hours in order to thermally crosslink. During this time, it is critical that the furnace be maintained at 200°C to prevent degradation of the film, and the wafer was periodically checked to ensure that the PAA film had not degraded.

The wafer now undergoes the first photolithography step, in which the windows to the substrate for all shapes are created. S-1818, a positive photoresist, is spin coated onto the wafer, with a time of 5 seconds at 300 rpm to spread, and 30 seconds at 2500 rpm to reach its final thickness of roughly 1.8  $\mu\text{m}$ . The wafer is then soft baked on a 115°C hotplate for 1 minute. Once this baking is finished, the wafer is loaded into a Karl Suss mask aligner along with the first photomask of the process. An exposure of 6 seconds on vacuum contact with a z-distance of -20 takes place. After exposure, the partial development step, as described above, occurs in a shallow dish of MF-319 developer for 35 seconds. After the wafer is rinsed in water and dried by a nitrogen gun, it is inspected using an optical microscope to ensure that the partial development occurred without causing the PAA layer to be prematurely exposed.

Next, the oxygen plasma ashing step, as described above, takes place. A YES Plasma Asher is used, which allows for oxygen plasma ashing sessions in intervals of nine minutes. The wafer is placed in the central part of the ashing chamber, and, after each ashing session, is checked under an optical microscope to observe how etching has progressed. To ensure a uniform exposure of the plasma to all shapes, the wafer is turned approximately 60 degrees in the ashing chamber before every session. Once the remaining photoresist and PAA in the developed windows of the wafer have been removed, the remaining resist layer is stripped using a spin coater, in which acetone is sprayed onto the wafer for 10 seconds, isopropanol for 10 seconds, and then dried for 30 seconds, all at 150 rpm to ensure a relatively low shear stress as compared to earlier spin coating sessions. This desire for a low shear stress originates with the desire to reduce the strain experienced by the exposed walls of PAA present along the sides of the etched windows. The improved mechanical strength of the PAA is another benefit gained from the earlier crosslinking of the layer, so what little stress it does experience from the spinner does not have a significant effect. Once again, the wafer is viewed under an optical microscope to ensure that a majority of the etched windows are not deformed or otherwise damaged before continuing the process.

From this point, until the removal of the PAA sacrificial layer at the end of the process, the procedure does not differ from the traditional SBSA process, except for moving the etching step for the titanium and copper seed layers from after the dip soldering step to just before the removal of the PAA. This keeps the PAA sacrificial layer beneath the seed layers protected from premature etching during the rest of the processing steps. It should be noted that postponing these etching steps did not appear to have any adverse effects on the process or the final structures.

Per the original SBSA process, a 17 nm adhesion layer of titanium and a 75 nm seed layer of copper are deposited on the etched PAA film using electron-beam evaporation. After this, the second photolithography step takes place, in which the faces of the eventual polyhedra and the central window are developed to expose the copper beneath the resist. The wafer is then placed in a copper electroplating bath in order for thick copper pads to deposit on the exposed seed layer. Afterwards, the resist is stripped with acetone and the final photolithography step takes place, in which each flat pattern is exposed in order to be covered with solder. LMA-117, a solder with a melting point of 47°C, is heated to a molten state in a small beaker on a hotplate set to 155°C. The wafer is cut into small 1-inch pieces, due to the size of the beaker containing the solder, dipped into solder flux, and then dipped in the LMA-117 while gently agitated for 90 seconds. After this, the resist layer is removed using acetone, while the copper seed layer and titanium adhesion layers on the rest of the wafer are removed using copper and titanium etchants, respectively.

In the final step, a solution of water and NaOH is prepared, as previously described. This 3:1 solution releases heat upon dissolution and, once this occurs, the wafer pieces are immediately immersed into the solution and agitated in order to remove the PAA sacrificial layer. After this, the sample is replaced into the solution and the heat caused by the mixture causes the solder to reflow prompting the polyhedra to self-assemble. After gently washing this sample with water and drying with a stream of air, the formed 3D structures are inspected under an optical microscope and, for more detail, with a scanning electron microscope (SEM).

### III. RESULTS AND DISCUSSION

During the thermal crosslinking of the PAA layer, it was found that the temperature plays an important role in the final quality of the film. Figure 3 shows a PAA layer after a thermal treatment in which the wafer was heated above 200°C, suggesting that heating above this temperature leads to degradation of the film around the outer edges. This author also considers that the uniformity of the PAA deposition, done via spin coating prior to the thermal crosslinking, may also play a part in this degradation pattern, as signaled by the degraded edges and relatively untouched center of these samples. This phenomenon was not of direct concern to this research, but further testing may reveal the exact cause. In samples without degradation, testing whether or not the PAA was sufficiently crosslinked was done through a simple dip test, in which the edge of the wafer was dipped into a shallow petri dish of water, blown dry with a nitrogen gun, and then visually observed for any discoloration along the dipped edge. If little or no discoloration was observed, the PAA film was determined to be sufficiently crosslinked.

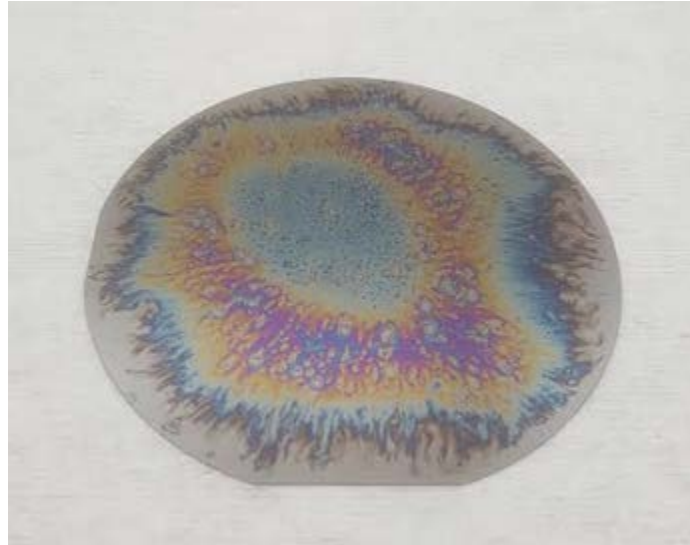


Figure 3. Photograph showing a degraded PAA film exposed to temperatures above 200°C.

During the partial development step in the first photolithographic patterning, the final development time of 35 seconds was determined empirically through repeated testing. Experiments showed that a development time greater than 40 seconds often led to the vulnerable PAA layer beneath the resist being exposed to the alkaline developer solution, which prematurely etches it. In previous experiments, it was found that the premature etching of the PAA layer would lead to undercutting of the resist mask causing the desired structures to be misshapen and oversized. Figure 4 shows an example of the undercutting that takes place if the windows are overdeveloped. Note that on the picture to the left, a faint ring can be seen below the resist layer which, after stripping, reveals itself to be the edges of the over etched window in the PAA, as seen in the picture on the right. Knowing this, the 35 second development time allows for as much photoresist to be removed as possible before the PAA layer is exposed, while still leaving enough time for the wafer to be rinsed and dried in order to stop the development



from further occurring, thus reducing the amount of oxygen plasma ashing required for the next step.

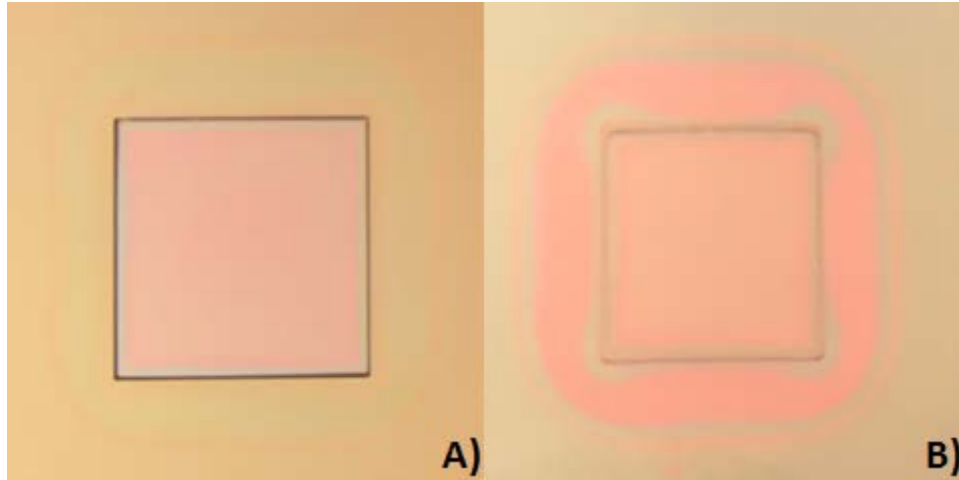


Figure 4. Optical micrograph of an overdeveloped and undercut square feature both A) before the resist strip and B) after the resist strip. (300  $\mu\text{m}$  side lengths)

During the plasma ashing of the partially developed shapes, the total ashing time varied from sample to sample, likely due to the varying amounts of undeveloped resist remaining from the previous step. However, these times usually ranged anywhere from 40 to 60 minutes, so this variance is not too restrictive. Figure 5 shows optical micrographs of the same shape and sample taken every nine minutes (our plasma asher is limited to zero-to-nine minute intervals) over 60 minutes. The last picture shows the bare wafer, seen as a deep blue color, observed after a final five minute ashing session, which signals the end of the ashing process. It should be noted that the final thickness of the un-exposed photoresist after this ashing should be about 1.0-1.2  $\mu\text{m}$  thick.

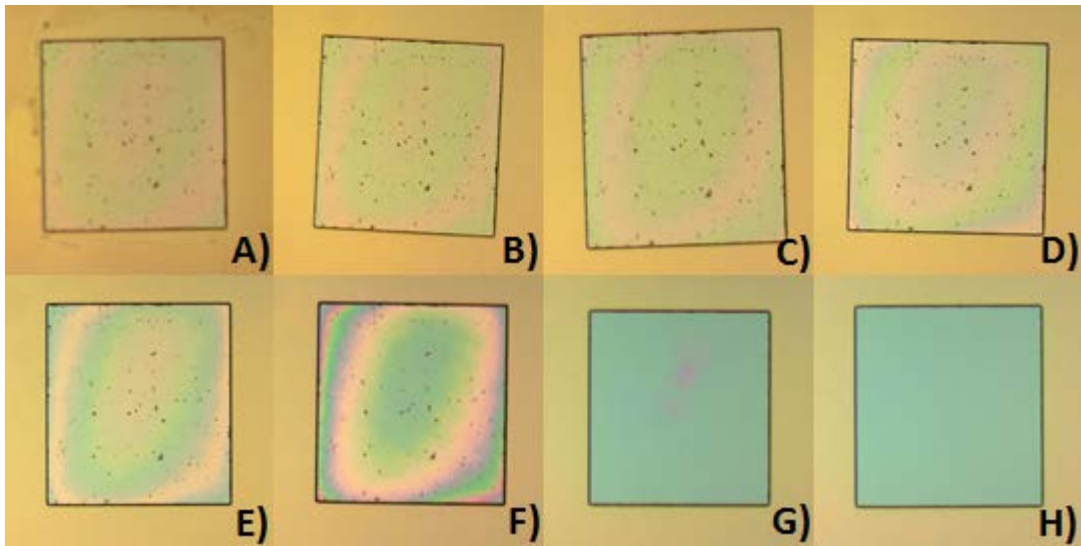


Figure 5. Optical micrograph of a square feature after having been etched via an oxygen plasma asher for: A) 0 minutes, B) 9 minutes, C) 18 minutes, D) 27 minutes, E) 36 minutes, F) 45 minutes, G) 54 minutes, and H) 60 minutes. (300  $\mu\text{m}$  side lengths)

It should also be noted that in earlier versions of this process, prior to the addition of the thermal crosslinking step for the PAA, the resulting resist strip revealed shapes with a streaking deformity. Figure 6 shows both a square window feature with clean edges that are suitable for continuing the process, and a square window feature with this streaking deformity. The exact cause of this deformity is still unknown, however, a suspicion about PAA fragility during stripping led to the eventual use of thermal crosslinking beyond its advantage in making the PAA layer less soluble in water. It was noted that the streaking occurred radially outward from the center of the wafer, leading to the thought it is the result of shear stress placed on the PAA by the stripping solvents. With this in mind, increasing the mechanical durability of the PAA was desired and eventually achieved through thermal crosslinking of the layer.

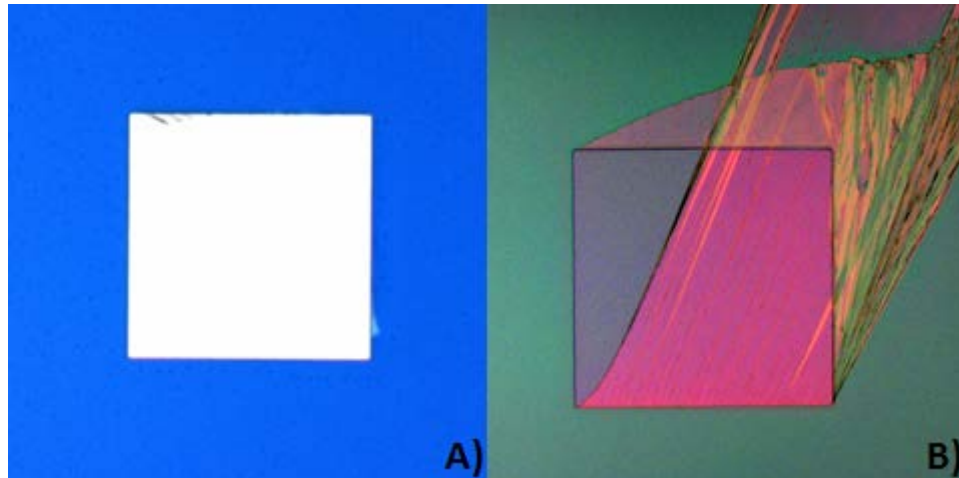


Figure 6. Optical micrographs showing square window features after a complete oxygen plasma ashing etch step and resist strip with A) clean edges that are suitable for continuing the process and B) a streaking deformity. (300  $\mu\text{m}$  side lengths)

One final note on the oxygen plasma ashing is that not all shapes in a given sample were completely etched. Shapes with a smaller area, such as triangles and squares, were etched faster than shapes with larger areas, such as heptagons and octagons, as seen in Figure 7. Residual PAA and photoresist in these larger shapes initially made them seem unusable, however final results, described later in this section, indicate that some of these shapes still folded without issue. Since these window shapes are to be used as the base of the polyhedra, it is hypothesized that having some small amounts of residual material left in them did not greatly affect their ability to act as an anchor to the substrate in the final folding step.

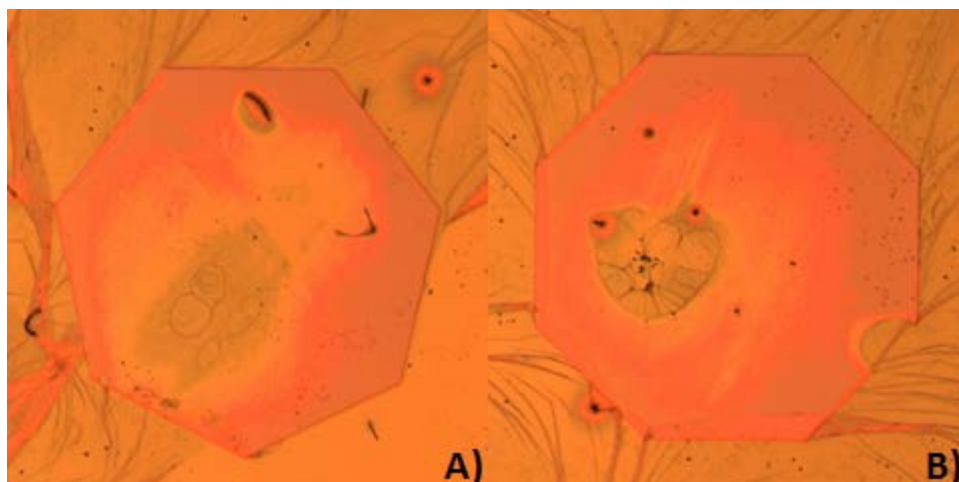


Figure 7. Optical micrographs showing incomplete PAA removal after the completion of oxygen plasma ashing and resist strip in: A) a heptagon and B) an octagon. Note that these images also show streaking deformities, as discussed above. (300  $\mu\text{m}$  side lengths)

From this point, all other steps until the final removal of the PAA sacrificial layer and subsequent folding follow similarly to the original SBSA process. Figure 8 shows SEM micrographs of successfully folded examples of the various 3D polyhedra along with their corresponding 2D flat patterns. In general, a fold was considered successful if it did not fall victim to any defects, examples of which are shown in Figure 9. In the sample from which these images were acquired, the resulting number of successfully folded structures was 57, thus giving a folding rate of 19%. It should be noted that this folding rate is not completely indicative of the true folding rate for the PAA SBSA method, as further experiments, with multiple samples produced without processing error, need to be performed to gain the true quality of the procedure.

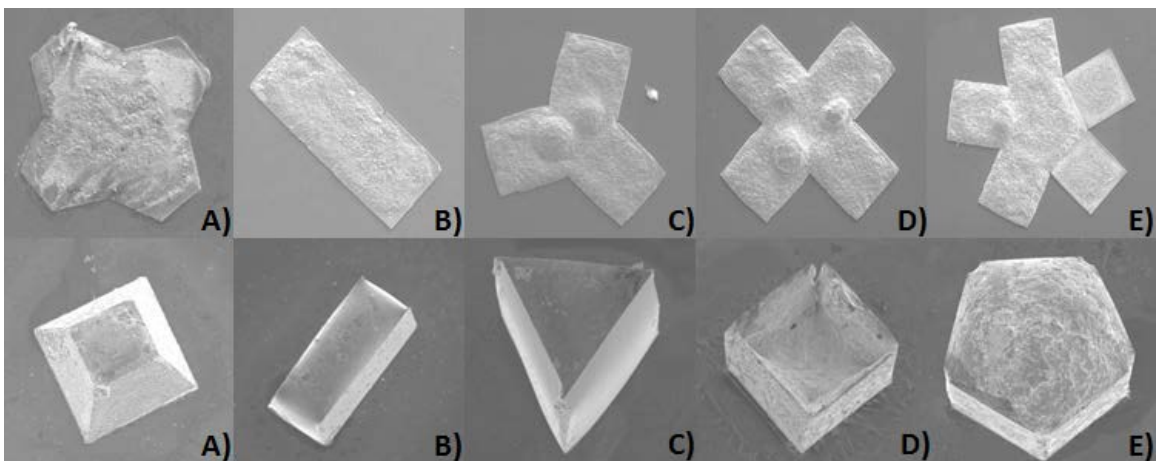


Figure 8. SEM micrographs of successfully folded 3D polyhedra below their corresponding 2D flat patterns including: A) truncated pyramids, B) open rectangular boxes, C) trigonal prisms, D) square boxes, and E) pentagonal prisms. (300  $\mu\text{m}$  side lengths)

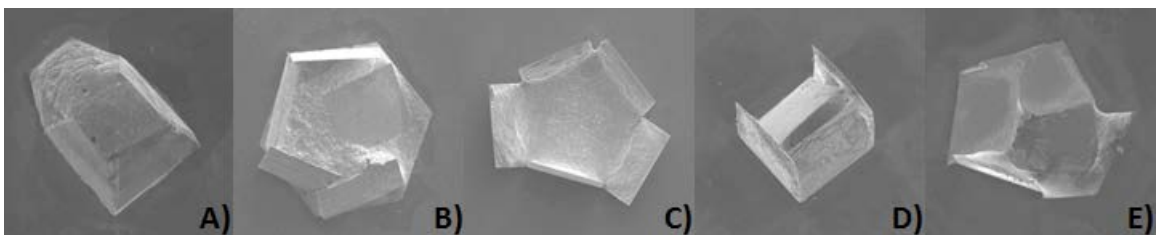


Figure 9. SEM micrographs of some notable failures, including: A) unfolded sides, B) missing sides, C) under-folded sides, D) over-folded sides and E) collapsed sides. (300  $\mu\text{m}$  side lengths)

In the sample from which the images in Figure 8 and Figure 9 were acquired, the resulting number of successfully folded structures was 57 out of 300, thus giving a folding rate of 19%. Table 1 shows the folding rates of each type of polyhedra present in the sample, with the octagonal prism having the highest folding rate of 27.8%. It should be noted that these folding rates are also not completely indicative of the true folding rates for the PAA SBSA method, but further experiments with more samples could produce more accurate values.

Table 1. The fraction of successfully folded structures and the resulting folding rates for each type of polyhedra present in the sample used for Figure 8 and Figure 9.

<i>Polyhedra Type</i>	Fraction of Folded Structures	Folding Rate
Open Rectangular Box	3/36	8.3%
Trigonal Prism	4/36	11.1%
Square Box	9/36	25.0%
Pentagonal Prism	8/36	22.2%
Hexagonal Prism	6/36	16.7%
Heptagonal Prism	8/36	22.2%
Octagonal Prism	10/36	27.8%
Truncated Pyramid	9/48	18.8%
<b>Total</b>	<b>57/300</b>	<b>19.0%</b>

#### IV. FURTHER APPLICATIONS

One of the major results of this research is the patterning method for PAA that was developed. The method, which relies on crosslinking of the PAA layer, performing a partial development, and using oxygen plasma ashing to create well-defined features, is one that might be applied for uses beyond the SBSA process. In this section, one such application which is currently being explored is detailed, with some preliminary results included.

Specifically, this application involves patterning crystal colloidal masks (CCMs) made from nanospheres. These CCMs are used in nanosphere lithography, a patterning technique in which nanospheres are deposited on a substrate and form a hexagonal close-packed structure. The interstices of this layer of nanospheres are then used as a mask for further etching or deposition steps to remove material, or deposit material upon, the substrate. From this fabrication method, it has been found that features such as nanodots and nanopillars can be easily made.<sup>31, 32</sup> Unfortunately, methods for patterning these CCMs, for instance, to include a microscopic feature amongst the nanoscale features, are few and can complications can occur. A major example of this includes pre-patterning the substrate prior to depositing the nanospheres, however, this restricts deposition methods for the nanospheres to those methods which can successfully allow nanospheres to deposit around such large pre-patterned features.<sup>33</sup> As such, spin-coating—one of the most inexpensive fabrication methods for CCMs—becomes nearly unusable in this instance.

With this limitation in mind, the idea arose use the patterning method for PAA, developed in the main body of this thesis, for patterning spin-coatable CCM layers. Specifically, since silica nanospheres are traditionally spin-coated on a substrate after being dispersed in

water, and since water is added in the PAA solution used in the PAA patterning method, the idea at hand is to disperse silica nanospheres in that solution, and then spin-coat them onto the substrate with the PAA. Upon doing this, the PAA would be crosslinked with the nanospheres embedded inside, and then the nanosphere embedded PAA layer would be patterned using the same partial development and oxygen plasma ashing method described previously. After the plasma ashing, the nanospheres in the exposed areas should be free from the PAA and thusly able to be pulled up with tape and removed. Finally, once the remaining photoresist is stripped away, the rest of the nanospheres should remain embedded in the PAA with the patterned features still present. At this point, ion-milling could be performed on the substrate and the nanospheres to pattern them, with the PAA layer offering little resistance to this etching technique. A potential process flow for this technique is shown in Figure 10 and a more detailed explanation of the technique is provided.

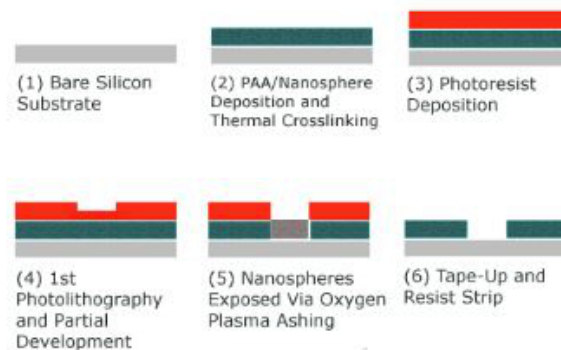


Figure 10. Process flow for crystal-colloidal mask embedded in PAA patterning process.

Following the process flow shown in Figure 10, a silicon substrate is cleaned via blowing away particulates using a nitrogen gun followed by a spin-coating a series of solvents. First, acetone for 10 seconds, a combination of acetone and isopropanol for 5 seconds, and only



isopropanol for 5 seconds, all at 300 rpm, and then finally spun dry for 30 seconds at 2500 rpm. After this basic cleaning, the wafer is ready for further processing.

In the next step, a 10% weight solution of PAA in water is prepared, and 300 nm diameter silica nanospheres are dispersed in this solution via shaking by hand until well mixed (roughly 5 minutes). At this point in time, via preliminary experiments, it appears that about 50 mg of silica nanospheres per milliliter of PAA/water solution is optimal. This solution is then spin-coated onto the silicon substrate at 1000 rpm and an acceleration of 950 rpm/s for about 1 minute. After this, the wafer should then be heated on a hotplate for 10 minutes at 115°C in order to remove most of the water, and then crosslinked via baking in a furnace at 200°C for 1 hour.

Now, a layer of S-1818 positive photoresist is deposited onto the wafer via spin coating with 5 seconds at 300 rpm to spread, and 30 seconds at 2500 rpm to reach its final thickness. The wafer is then soft baked on a 115°C hotplate for 1 minute. Once this is finished, the wafer is loaded into a Karl Suss mask aligner along with a photomask. This is the same photomask that was used in the first step of the SBSA process containing the patterns for differently shaped windows. An exposure of 6 seconds on vacuum contact with a z-distance of -20 takes place. After exposure, the partial development step, as described previously, occurs in a shallow dish of MF-319 developer for 35 seconds. After development, the wafer is rinsed in water and dried by a nitrogen gun.

In the next step, oxygen plasma ashing takes place repeatedly on the wafer until the exposed parts of the PAA layer are removed. This step, similar to the SBSA process, takes about 45 minutes to complete, with repeated checks using an optical microscope to inspect progress. Eventually, the nanospheres should become visible as small specks on the substrate indicating groups of nanospheres. After the PAA has been completely removed, a resist strip takes place in

which the remaining photoresist is removed. Finally, a procedure using tape for removing remaining nanospheres is performed. Kapton tape was cut into small pieces, placed over the etched features, pressed down gently using fingers and/or tweezers, and then pulled up. This sometimes requires multiple tape pulling to completely remove all the visible nanosphere clusters from the features, as seen under the optical microscope. Figure 11 shows some optical micrographs of a rectangular and a pentagonal feature before and after the tape-pull step has occurred.

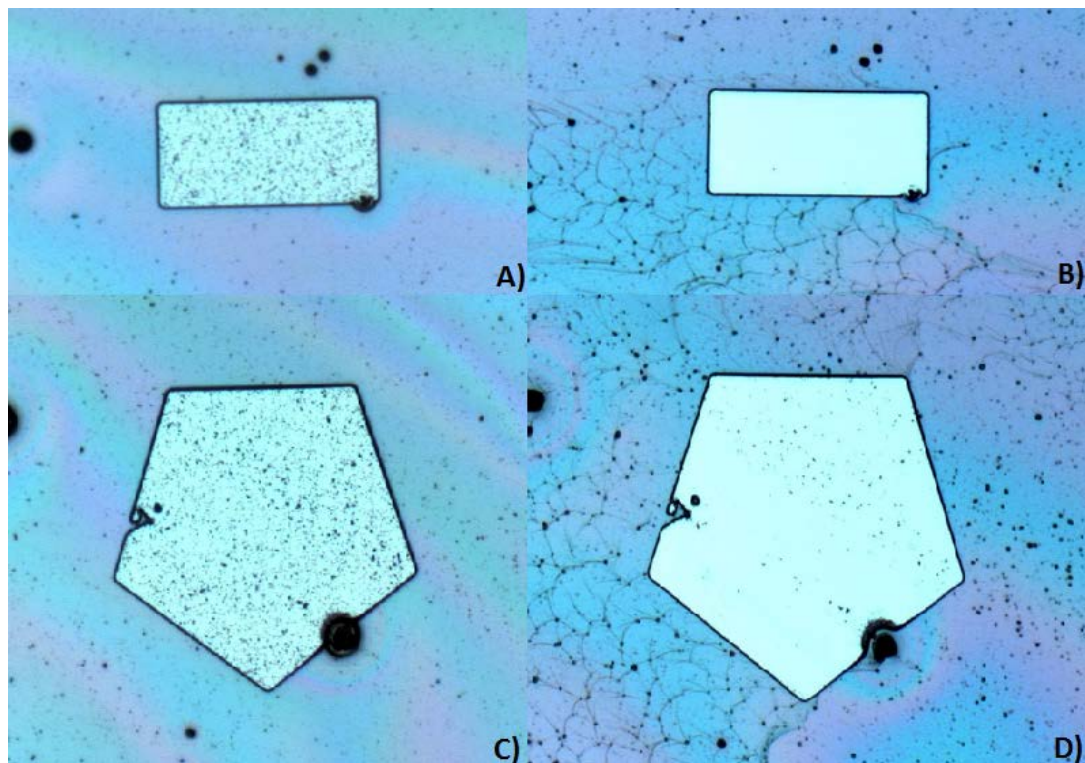


Figure 11. Optical micrographs of some preliminary successes of the process flow seen in Figure 10, showing: A) a rectangle before taping-up the nanospheres, B) a rectangle after taping up the nanospheres, C) a pentagon before taping-up the nanospheres, and D) a pentagon after taping up the nanospheres. (300  $\mu\text{m}$  side lengths)

Naturally, more work needs to be performed to confirm the viability of this idea. An important step will include examining these features and the nanospheres using SEM to get clear images of the CCMs. This should lead to information on whether or not they are being formed, and whether they are actually being removed by the tape-up step. Furthermore, fine-tuning of the procedure must take place to find the truly optimal parameters for both putting down these CCMs and properly patterning the nanosphere embedded PAA layer. Future tests should help to answer these questions. Ultimately, it may also help to perform a final nanosphere lithography etching step on a given sample via ion-milling or another physical etching technique in order to see whether the PAA layer causes any significant problems at that point. Potentially, if the PAA layer is a problem, further steps may need developing for removal of the remaining PAA from the remaining nanospheres in the CCM.

## V. SUMMARY AND CONCLUSIONS

From this work, a method by which 3D polyhedral structures can be self-assembled from 2D flat patterns on a silicon substrate using a PAA sacrificial layer is described. Incorporating PAA required many process modifications due to the water-soluble nature of the polymer. Specifically, by thermally crosslinking the PAA layer, and then patterning it using a partial development scheme combined with plasma ashing, the steps of the traditional SBSA process can be followed until the end of the process flow when NaOH is used to etch the PAA and subsequently cause the shapes to fold. This method is meant to be a safer alternative to performing the SBSA process, which utilizes a SiO<sub>2</sub> sacrificial layer etched by a potentially hazardous material, HF acid. It is our hope that this research also contributes to materials processing knowledge that can be useful for applications requiring patterned PAA films. The experimental results provide evidence that the modified method is capable of producing 3D structures similar to that of the well-studied SBSA approach. Future research includes repeating the PAA SBSA process multiple times successfully in order to compare the yields of folded shapes to that obtained by the original SBSA process. Furthermore, replacing the sacrificial layer with other polymers could result in further alternatives to the SBSA process but, as the use of PAA shows, a direct substitution of materials is not as simple as one might initially assume.

Furthermore, a topic for future research has been investigated that builds upon the main focus of the work described in this thesis, a technique for patterning PAA layers. The intention of this research is to advance the use of spin-coating to form crystal-colloidal masks for nanosphere lithography by introducing a novel method for patterning layers of nanospheres. More

specifically, the belief is that by embedding the nanospheres in a solution of PAA and water, and then spin-coating that mixture onto a substrate, the same steps for patterning PAA sacrificial layers can be performed to pattern crystal colloidal masks. Upon performing the same crosslinking, partial development, and oxygen plasma ashing steps, features of exposed nanospheres can be taped-up and, thus, leave behind a patterned layer of nanospheres embedded in PAA. Further experiments involving this idea need to be performed to determine viability. Preliminary results indicate promise for this technique.

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## APPENDIX A. Copper Plating Bath Set-Up Instructions

- 1) Collect the following pieces of equipment and inspect for any immediate damage or problems:
  - a. Safety Equipment—Primarily, a lab coat, latex gloves, acid gloves, close-toed shoes, safety glasses, and a face mask
  - b. Bath (1)—Main body with attached stand
  - c. Electrode Holder (1)—Piece of clear plastic with large notches
  - d. Bath Head (1)—Piece of clear plastic with a circular pattern of holes used to project solution flow
  - e. Plastic Tubing Without Stop Valves (2)—Plastic tubing that does not have any valves for stopping the flow of fluid
  - f. Plastic Tubing With Stop Valves (2)—Plastic tubing that does have valves for stopping the flow of fluid
  - g. Filter With Filter Housing (1)—Large cylindrical filter housing with a filter inside



- h. Ring Stand With Ring (1)—Tall ring stand with a ring on it over the wide open area of the base of the ring stand
  - i. Pump (1)—Small pump with a cord
- 2) Place the Bath on the right-hand side, inside of the fume hood. Make sure that the piping coupler on the bottom has its opening facing to the left.
- 3) Place the pump on the left-hand side, inside of the fume hood. Make sure that the piping couplers on it are facing outward of the fume hood. Check to make sure the electrical cord can reach the outlets on this side of the fume hood. Do not plug in the power cord yet however, as running the pump dry can damage it!
- 4) Place the ring stand in the middle-right portion, inside of the fume hood. Place the filter housing, with the filter inside, on top of the ring stand. Have the bottom outlet of the filter housing go through the ring on the ring stand and lean the rest of the filter housing on the ring stand. It may be useful to use zip-ties or some other sort of securing device to further attach the filter housing to the ring stand. Finally, place a plastic beaker under the bottom outlet of the filter housing in preparation for any potential leaks that could ever occur.
- 5) Find the plastic tubing without stop valves that has a couple on both ends of it. Gently turning the Bath on its side, attached one end to the piping coupler on the bottom of the bath. Secure this connection using two wrenches to turn in opposite directions. Leave the other end of the tubing, with the other coupler, unattached to anything for now.
- 6) Now, turning the Bath back to its original upward position, place the Electrode Holder on the bottom, and the Bath Head inside, such that the holes of the Bath Head face to the left.

- 7) Find the plastic tubing without stop valves that only has one coupler on one end, and no coupler on the other. Stick the end without the coupler into the wider tubing of the Bath Head deeply and securely. Then attach the coupler end to the right hand outlet of the filter housing at the top. Be sure to tighten the coupler with wrenches.
- 8) Find the plastic tubing with a stop valve that has that stop valve on one end of the tube, and a coupler on the other. Attached the stop valve end to the coupler of the plastic tubing without a stop valve that was attached to the bottom of the Bath. This should create one long tube, with a stop valve in the middle, which stretches from the bottom of the Bath. Now attached the coupler end of the tube to the input of the pump, which should be coming out of the front of the motor and facing outward of the fume hood. Secure the connection to the pump with wrenches, but do not yet secure the connection between the stop valve and the plastic tubing coming out from under the bath—this connection will be used in a later step for priming the pump, so securing it is not necessary yet.
- 9) Find the final piece of plastic tubing with a stop valve and attach one end to the left-side outlet of the filter housing. Then attach the other coupler on the other end of the tubing to the outlet of the pump, which should be sticking out of the side of the pump in the upper-right direction. Secure both of these connection with wrenches.
- 10) At this point, you may have found that some of these connection have put stress on the various parts of the pumping system—such as the filter housing or pump itself. If this is the case, it would be good to go through and undue some connections in order to twist the tubing such that this stress is removed. Ideally, the pump should be able to sit flatly in the fume hood, and the filter housing should be securely against the ring stand without threatening to tip over.

- 11) Now, with everything in place, fill a beaker with DI water and fill the bath partially with DI water—usually just a couple inches full will do. This will act as our fluid to be pumped in order to both prime the pump and check for leaks—as opposed to filling the bath with Cu-Plating Bath Solution and running the system, which can be dangerous in case the system does have leaks or backs up somehow. On this note, do not be alarmed if the piping attached to the bottom of the Bath begins filling with some fluid—this is natural due to gravity.
- 12) With the Bath filled partially with DI water, we will now have to prime the pump—meaning that we must add some liquid to the pump the “jumpstart” it. This is done because this pump, like many of its kind, is not powerful enough to pump gases such as air, so the liquid to be pumped must be forced to its inlet to get the process started. To do this, undue the piping between the stop valve of the plastic tubing attached to the inlet of the pump, and the coupler of the plastic tubing on the bottom of the bath it was connected to. As mentioned previously, this connection should not have yet been secured with wrenches, and should be easy enough to undue. Now, using another beaker of DI water, begin gently pouring DI water into the tubing that leads to the inlet of the pump. This can be difficult due to capillary forces forming a droplet of the opening of the valve and stopping you from pouring in more DI water, so try to create a small and steady stream at the mouth of the tubing so that this does not occur. Stop once the tubing has been filled and water reaches up to the mouth of the tubing.
- 13) Now re-secure the connection between the stop-valve and the coupler, and further secure this connection with wrenches.

14) Now, with the pump filled with some DI water at its inlet, you can insert the power cord into the outlet, which should turn on the pump. If everything is working correctly, you should see the DI water being pumped through the tubing and up to the filter housing, where it will take a moment to fill the housing before continuing on over to the Bath Head. At that point, it should be coming out of the holes in the Bath Head, and draining into the tubing at the bottom of the Bath—completing the cycle. If this is not occurring, and DI water is remaining inside of the tubing, turn off the pump immediately, and review the steps above. Potential problems could be leaks, or there not being enough water in the inlet of the pump to prime it.

15) With the pump system now running smoothly, check for any leaks in the system. If any are found at connections, tighten those connections. If there are holes in the tubing itself, stop the pump and try to fix it with tape or even a beaker to catch the leak. Such damaged tubing should be replaced as soon as possible.

16) See Figure 12 below to check your setup:

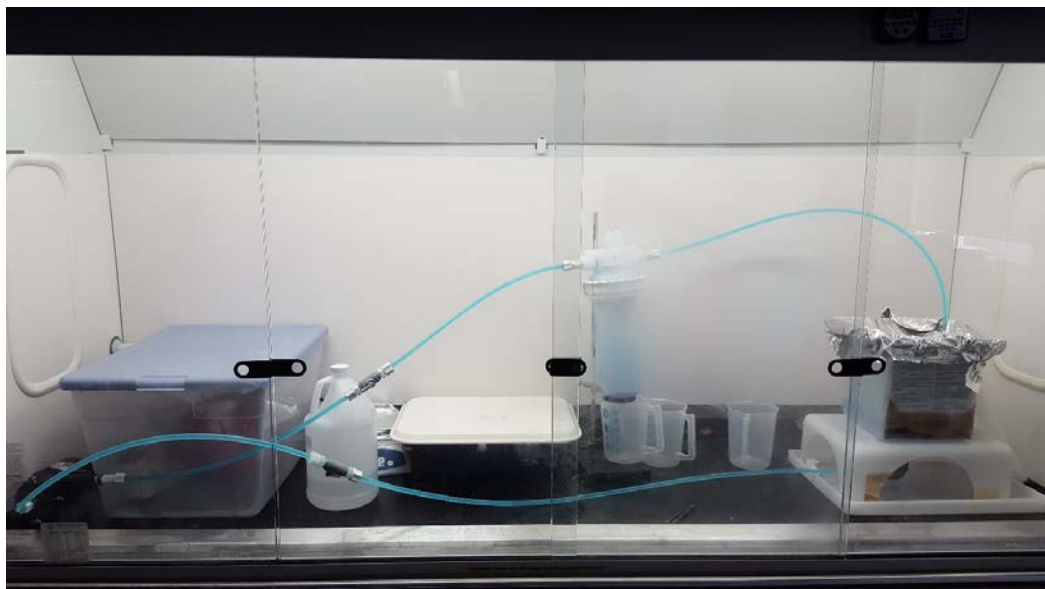


Figure 12. Full set-up for custom copper plating bath in laboratory used for SBSA process.

## APPENDIX B. Copper Plating Bath Operation Instructions

- 1) To begin, inspect the level of the plating bath solution to insure that it is 1-2 inches below the lip of the top of the plating bath. This is that any wafers placed into the bath are completely submerged. If, the plating bath solution is not at the appropriate level, simply add more plating bath solution until that level is reached. This may take multiple people or even a small hand-pump to do, as the container for the plating bath solution can be quite bulky and heavy to use.
- 2) Before plating a sample can begin, an anode conditioning must occur. To perform this, the anode, a copper plate, and a dummy sample, a smaller copper plate, must be placed in a Pyrex dish and submerged in copper etchant for 5 minutes to clean them. Next, the plates must be washed with DI water, and then submerged in another Pyrex dish filled with low concentration sulfuric acid for 1 minute for further cleaning. Now, after taking out the copper plates and washing them with DI water, they are ready to be placed inside the copper plating bath. The anode plate must be placed on the nozzle side of the plating bath in a vertical and upright position. Next, the dummy plate must be mounted on the sample mount and submerged into the plating bath facing the anode, but about six inches apart. Now, the power supply must be attached to these plates, with the anode attached to the positive lead, and the sample holder being attached to the negative lead. Then the power supply must be run at a current density of about  $4.735 \text{ mA/cm}^2$  for at least 30 minutes.

3) Now, with the anode properly conditioned, the actual sample can be placed in the sample holder and submerged in the copper plating bath. With this sample in place, once again the power supply is run again at a current density of about  $4.735 \text{ mA/cm}^2$  until the copper has been properly built up to a thick enough level. This can be determined by checking the sample periodically under an optical microscope. Upon the sufficient thickness being reached, the sample must be cleaned with DI water, and stored away for further processing. The anode can then be removed and washed with DI water as well, then dried and stored away for further use. The plating bath must be covered with aluminum foil, or a plastic cover, to ensure that the plating bath solution does not evaporate too quickly.