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Integrating Nanosphere Lithography in Device Fabrication

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# Abstract

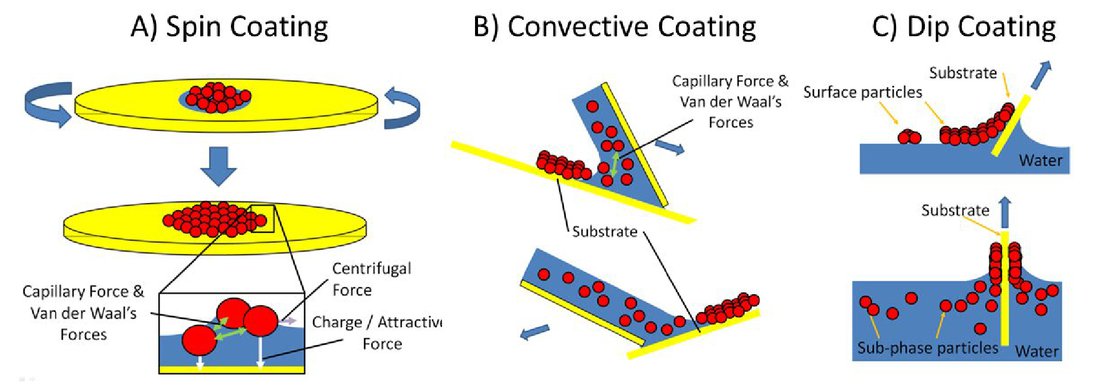
This paper discusses the integration of nanosphere lithography (NSL) with other fabrication techniques, allowing for nano-scaled features to be realized within larger microelectromechanical system (MEMS) based devices. Nanosphere self-patterning methods have been researched for over three decades, but typically not for use as a lithography process. Only recently has progress been made towards integrating many of the best practices from these publications and determining a process that yields large areas of coverage, with repeatability and enabled a process for precise placement of nanospheres relative to other features. Discussed are two of the more common self-patterning methods used in NSL (i.e. spin-coating and dip coating) as well as a more recently conceived variation of dip coating. Recent work has suggested the repeatability of any method depends on a number of variables, so to better understand how these variables affect the process a series of test vessels were developed and fabricated. Commercially available 3-D printing technology was used to incrementally alter the test vessels allowing for each variable to be investigated individually. With these deposition vessels, NSL can now be used in conjunction with other fabrication steps to integrate features otherwise unattainable through current methods, within the overall fabrication process of larger MEMS devices. Patterned regions in 1800 series photoresist with a thickness of ~700nm are used to capture regions of self-assembled nanospheres. These regions are roughly 2-5 microns in width, and are able to control the placement of 500nm polystyrene spheres by controlling where monolayer self-assembly occurs. The resulting combination of photoresist and nanospheres can then be used with traditional deposition or etch methods to utilize these fine scale features in the overall design.

# 1.INTRODUCTION

Nanospheres and their ability to form self-ordered monolayers have been studied for several years. For many applications however, it would be beneficial if a means were available to better control the location and orientation of these monolayers of nanospheres. The nano-scaled dots produced from this form of nanosphere lithography (NSL) have been used in many applications. Typically these particles are as a metallic growth medium for structures such as carbon nanotubes or nanowires of various compositions. While generally patterning has been demonstrated through mass deposition of nanospheres, patterning entire surfaces, and selectively removing unwanted dots, in some applications that may not be ideal or even possible. In these instance, it may be beneficial instead to have the ability to control nanosphere placement prior to using them in lithography.

To explore this topic, first the current state of nanosphere deposition technologies and methods were reviewed to determine the optimal method to pursue. Much of this work has been recently summarized by Dr. Wang from the University of Texas at Arlington.1 In this work Dr. Wang et al outline many basic principles, including particle behavior and the spacing observed due to surface of particles and substrate, forces in action, etc. Also, this paper discussed how these apply to several techniques of application including primarily spin-coating, dip-coating, and evaporative techniques. While much of this summary will be referred to throughout this paper, the three most applicable deposition techniques are shown in Figure 1.

Figure 1. Three methods of nanosphere self-assembly including spin coating (A), convective coating (B), and dip coating (C).



Based on this work and previous research efforts,2,3 we summarized that while the equipment for spin coating may be readily available, and with some specific combinations of materials can produce good results, in general this method is unpredictable and results are difficult to repeat reliably. Spin coating was designed to work well using materials which were created with very adhesive properties and engineered to possess a specific viscosity so that through spinning at a specific rotational speed, we can induce a repeatable thickness (i.e. photoresist). Nanospheres on the other hand are already set in thickness, and controlling viscosity and adhesion can be difficult. To illustrate this consider the forces at work in spin coating as shown in Figure 1, part (A). As discussed by Wang et al, self-assembly of nanospheres depends on controlling multiple forces not only between spheres, but also between the spheres and the surface. Particles must have enough attraction to the surface to not be dislodged under centrifugal force, but not so much that they do not reflow into a uniform layer. Thus, methods of deposition which utilize liquid-air interface depositions are far easier to accomplish for patterning these spheres.

Another common method of nanosphere deposition is evaporative.4,5 In this technique, a liquid containing nanospheres is allowed to evaporate, and at the interface, capillary forces readily form small areas of monolayers (an experiment which is easy to observe in a laboratory with a simple microscope and liquid suspension of nanospheres). Several issues arise if this method is applied to forming large, regularly patterned areas. First is maintaining enough particles near the interface to support a uniform monolayer and replenish particles as they are drawn out of solution, but not too much which might result in either multilayer clumping. Also, the geometry of a drop of water presents another challenge.4 The boundary of a droplet is circular, and while at large radii this appears to be linear enough to form rows of particles, as the drop evaporates the radius or curvature decreases and this in turn changes the orientation of the interfaces relative to each other. As these regions grow together, they are not aligned to one another and too many particles have been deposited to be easily re-ordered to match a single alignment.

We can however use this method of self-assembly and avoid these issues if we look at the third method to be discussed, dip-coating. This method involves slowly passing the substrate along the liquid interface and either transferring a floating monolayer from the surface of the liquid to the substrate as shown in Figure 1, part (C), or forming of the monolayer during extraction through capillary forces as shown in Figure 1, part (B). Both of these methods use a substrate held at an angle to the liquid’s surface, resulting in a linear liquid-air interface. This eliminates the geometry issue of evaporative deposition discussed.1 Using this theory, the adhesion issues which arise with spin-coating are less difficult to manage, but unlike spin-coating we do not have readily available laboratory equipment necessary to carry out this kind of deposition. When considering how to build such an apparatus, the first difficulty is how to design the mechanical movement which accomplishes a slow, steady passing of the substrate through the surface of the liquid to accomplish the assembly, but gently enough to not interfere in self-assembly. To counter this obstacle, various authors have proposed a variation of the dip-coating technique in which the liquid is drained and the surface falls around the stationary substrate instead of attempting any mechanical motion.6 This technique was outlined by several authors, including one publication by HP laboratories in which this was one step of a more complex fabrication process.6 While many details in these efforts are vague, the one challenge which appears to be common is how to physically design the deposition apparatus.

Understanding how these self-assembled layers form and how to accomplish self-assembly is only part of the overall goal of this effort. The second phase of the process is then to address how to control the placements of these nanospheres in a useful manner. Several authors have presented various methods using nanospheres as part of lithography, typically manipulating the inter-sphere holes with plasma ashing or reactive ion etching, then using the result in a typical lithographic manner. However, few if any have presented any attempts at controlling nanosphere placement prior to using them in this way.

# 2.METHOD

## 2.1 Building a Drain-Coating Deposition Vessel

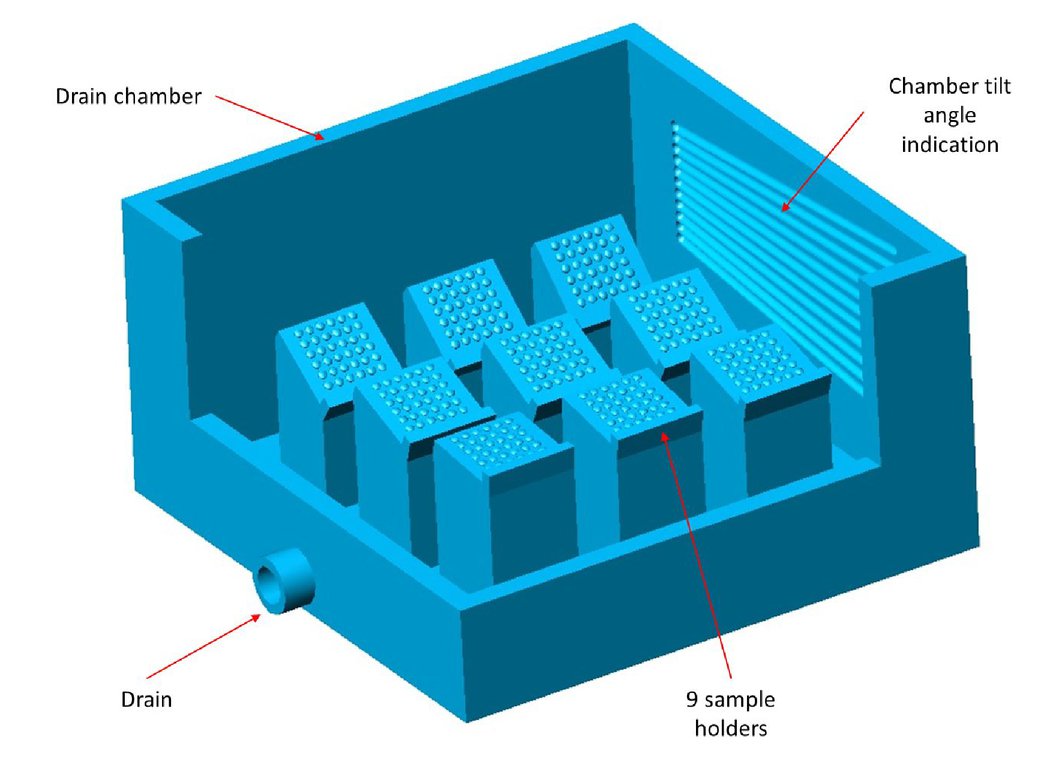
Draining methods have been published for several years, but in all cases the limiting factor appears to be the apparatus used to accomplish the transfer. To understand this, consider the conclusions presented by Wang et al. To successfully transfer spheres to any surface requires the control of many factors including:

* Sphere diameter (specifically how it relates to many of the factors below)
* Sphere composition (material properties and more importantly, surface attractions and repulsions, material density, ability to carry a charge, etc.)
* Attraction between spheres (enough attraction to promote layer formation but not too much which would then result in disorganized clumping materials)
* Attraction between the spheres and the substrate (enough attraction to prevents sphere movement after deposition but not too much to prevents spheres from repositioning)
* Fluid viscosity (which in turn controls curvature of the meniscus at the liquid-substrate interface, and any given curvature is only ideal for specific sphere size)
* Angle of the substrate to the surface of the fluid (which influences both rate of sphere removal as well as the geometry of the meniscus).
* Rate of fluid removal (quick enough to promote layer formation but not so fast that spheres are unable to diffuse quickly enough to replace spheres which have been deposited and further support layer growth).

Many of these factors are controlled through material selection, and the rest addressed by designing very specific vessels to accomplish the transfer of nanospheres. For all experiments in this paper, the nanospheres used were made of polystyrene with a diameter of 500 nm. These were supplied pre-suspended in deionized water which was diluted (1:1) with an ethanol solution. This ethanol solution contained trace amounts of Triton-X.7,8 The substrate used was silicon, in some cases pre-cleaned with an ammonia hydroxide solution in some cases simply cleaned with methanol. The carrier fluid in all cases was deionized water. The vessels were designed using readily available, computer aided design (CAD) software and fabricated using commercially available 3-D printing technology. The printed material was acrylonitrile butadiene styrene (ABS) plastic printed through heat extrusion, and sealed with acetone and/or silicon to prevent leaking as well as repel the nanospheres present. Several iterations of these vessels were built and tested, the highlights of which will be discussed below.

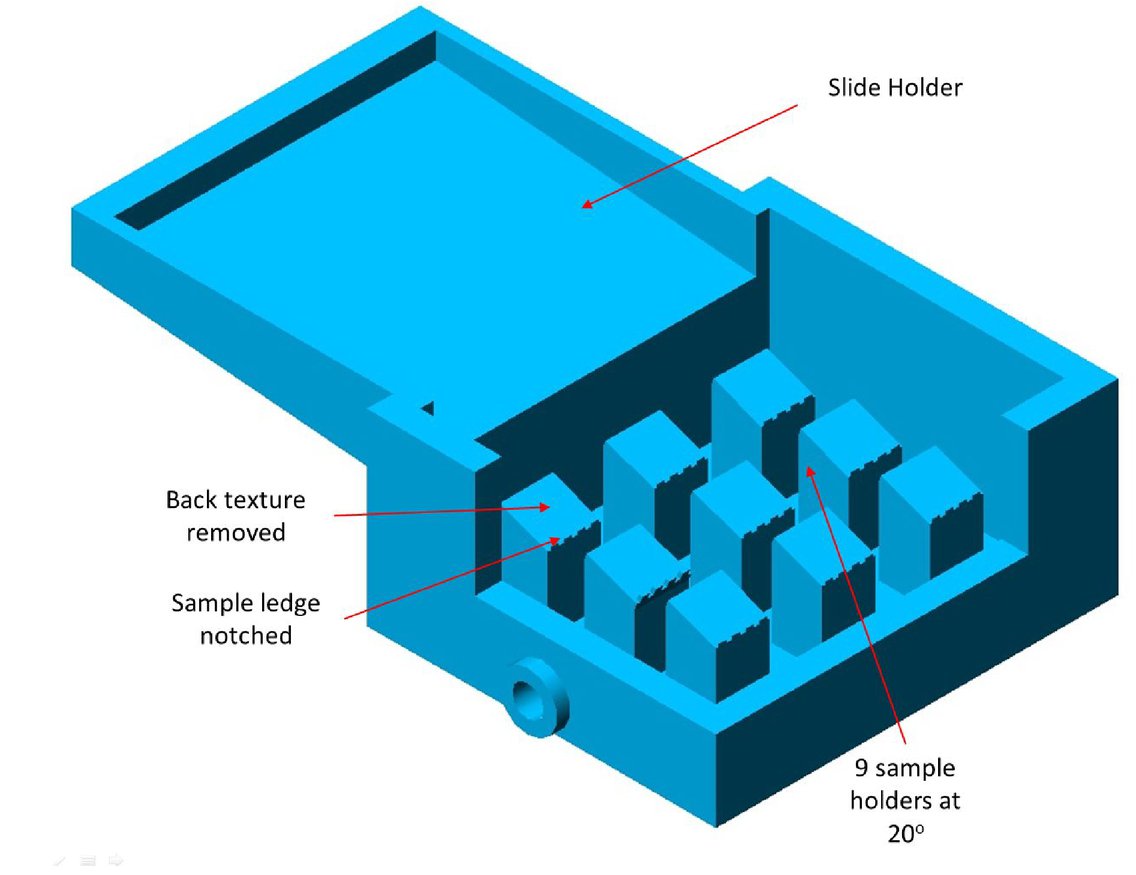
The first vessel which was fabricated was designed to test the optimal angle between the substrate and the surface of the fluid. This vessel is shown in Figure 2. The nine sample holders were each a different angles ranging from 5° to 45° of inclination. This vessel was filled with deionized water, and the silicon substrates placed on the holders. The nanosphere solution was then transferred to the surface of the carrier liquid. By then slowly draining the liquid, transfer to the samples was accomplished.

Figure 2. Drain-coating deposition vessel design (with cutout) showing nine sample holders, each varying in inclination angle ranging from 5 degrees to 45 degrees relative to the liquid surface.



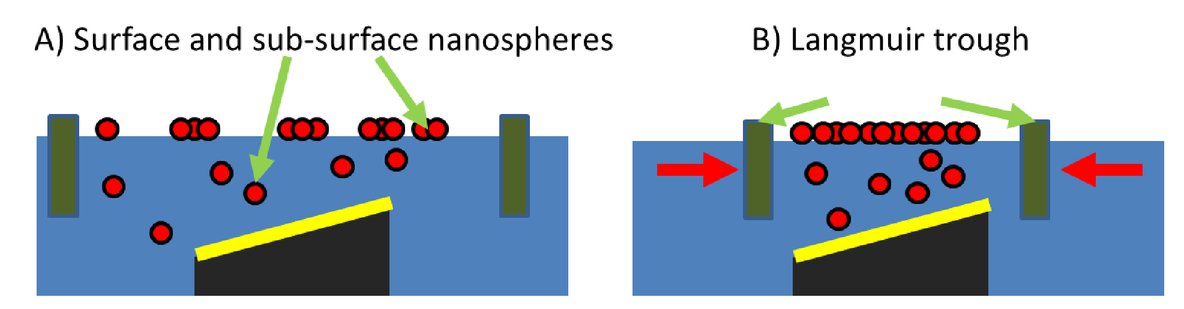
The next version is a vessel which has fixed the sample carriers angle to the surface, and was also modified to provide better drainage on each holder by removing the back texturing and notching the bottom lip on each pillar, shown in Figure 3. Additionally, the vessel contained a ledge on which glass slide could be placed to aid in loading the surface with nanospheres. The glass slides serve as a transfer mechanism for the nanosphere solution to the carrier fluid.

Figure 3. Drain-coating deposition vessel design (with cutout) showing 9 sample holders, each varying in inclination angle ranging from 5 degrees to 45 degrees relative to the liquid surface.



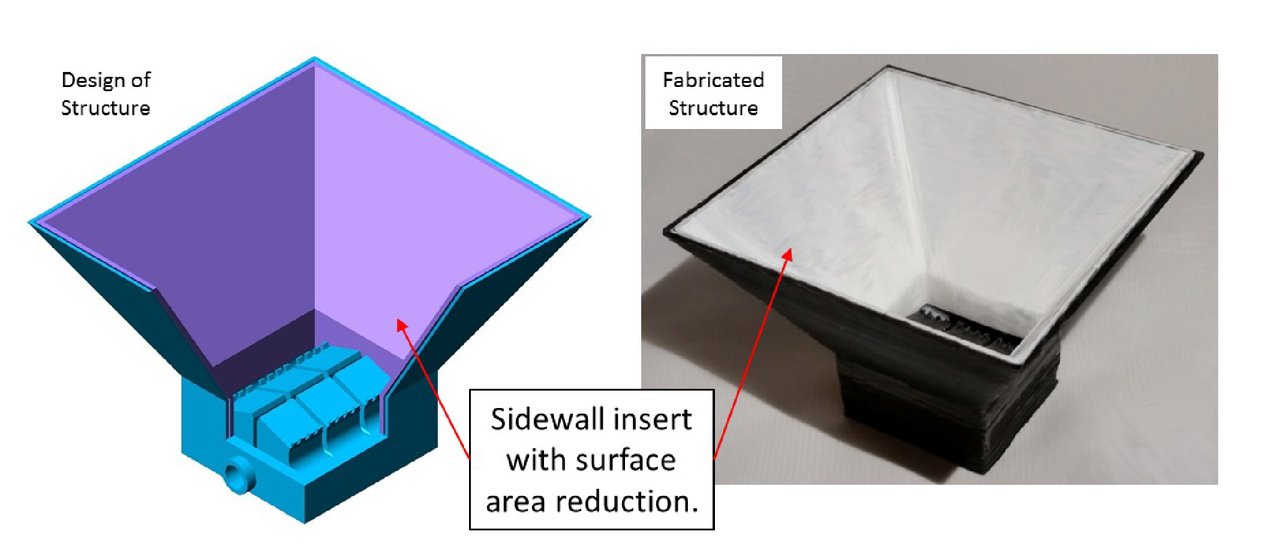
While the addition of the glass slide holder aids in loading nanospheres to the surface of the carrier fluid, the question still remains regarding the optimal surface density of particles and how to aid in formation of monolayers prior to deposition. Several research efforts have addressed this question through the use of a device called a Langmuir trough. The principle behind how this technique is used is shown in Figure 3.9 While a typical trough incorporates moving walls which constrict the surface area, this approach involves complications regarding how to include the moving parts and control their motion, maintain the seal on the vessel, etc. Instead, surface area compression through other means was investigated.

Figure 4. Principle of operation of a Langmuir trough; nanospheres deposited onto surface (top) can be induced into more tighter patterning by compression of surface area resulting when one of both of the trough barriers are moved..



To mimic the effects of a Langmuir trough, a vessel with a sloped upper surface was investigated and is shown in Figure 5. The concept of operation of this sloped funnel is that as the fluid is removed, surface area reduction occurs which will accomplish the same surface area compression as with a traditional Langmuir trough. This design has no moving components and accomplishes compression in both the x and y direction, but the amount of surface are reduction is not ‘tunable’ as it would be with a typical trough.

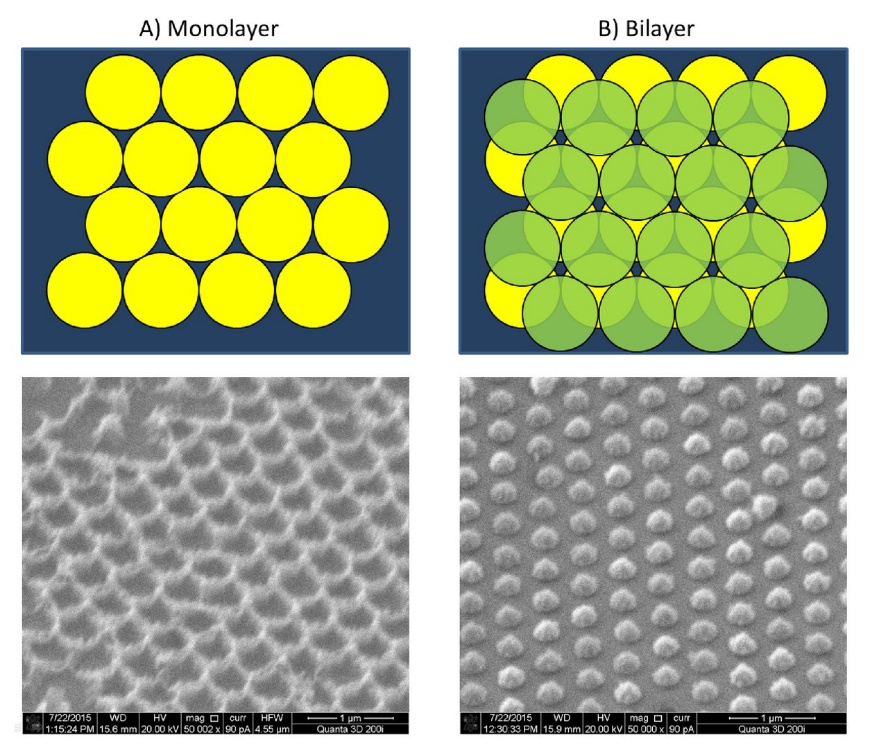
Figure 5. Funnel shaped deposition vessel which compresses fluid surface area through the draining process.



## 2.2 Patterning Nanosphere Depositions

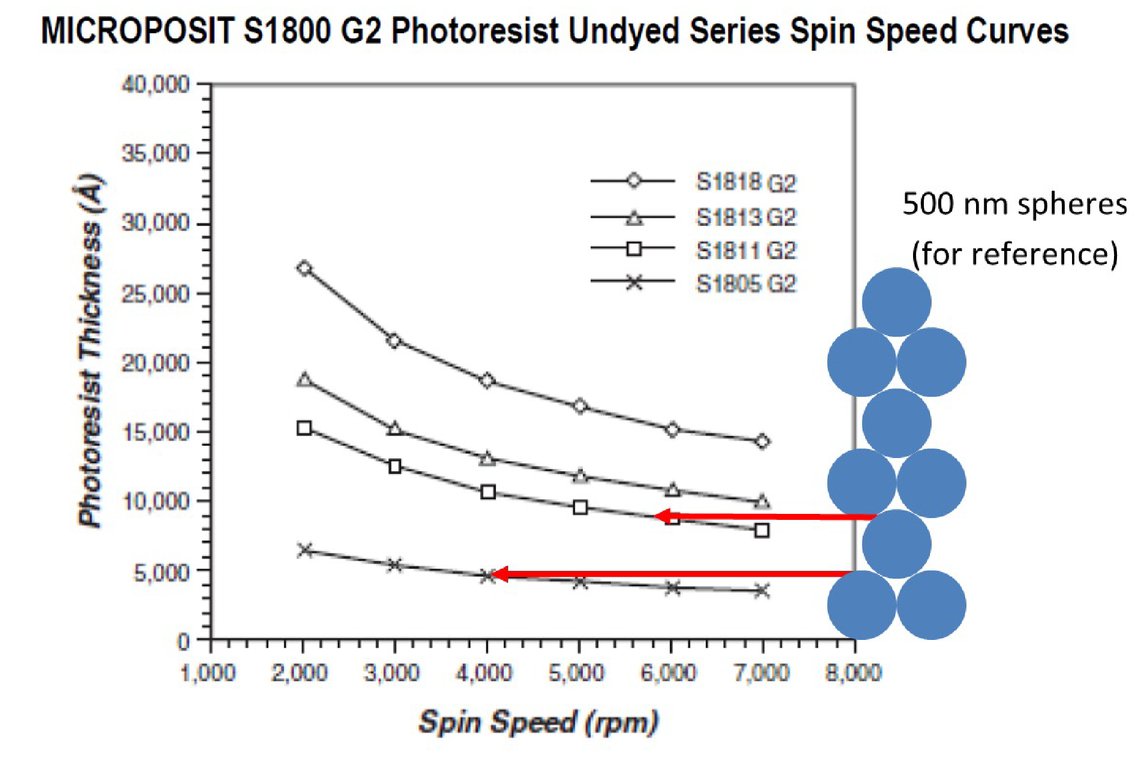
With these vessels available to accomplish nanosphere self-patterning, the second part of this effort is to evaluate if these depositions can be used with other patterning techniques to control nanosphere placement. This may be precise control of a small number of spheres in a monolayer, or possibly larger areas with multiple, regularly patterned layers. As indicated by Wang et al and others,1,10 both monolayers, bilayers and possibly even higher numbers of layers may prove useful as a lithography pattern. To better understand this, refer to Figure 6. In the case of a monolayer (A), the inter-sphere voids provide a hexagonal pattern for depositions made between particles while a bilayer (B) every other void is blocked by the second layer, resulting in a triangular pattern. If a third layer were to be present, there is a 50% chance that it would simply lie directly over the first layer and a 50% chance that it would block the remaining holes. Thus monolayers and bilayers seem to be the two most useful structures in nanosphere patterning.

Figure 6. Illustration of nanosphere placement for both a Monolayer (A) and Bilayer (B), and resulting patterns after RIE with sputtered gold. In the case of a monolayer, hexagonal patterning results compared to a bilayer, which results in a triangular pattern.



The goal of this effort is to capture these patterned layers in confined regions of photoresist, the next consideration is the type and thickness of that photoresist. Since we’ve established that for this effort we’ll be using nanospheres with a diameter of 500nm, one possible combination of photoresist selections is shown in Figure 7. The curve is that provided by Dow Chemical Company for their Microchem 1800 series of photoresist.11 One the right, the relative sizes of 500nm nanospheres stacks are shown with the anticipated layer heights. If the goal is to only capture monolayers or bilayers of nanoparticles, 1805 and 1811 photoresist will produce the appropriate thicknesses at the spin speeds indicated on the Figure.

Figure 7. Comparison of 1800 photoresist data sheets compared to 500nm sized nanospheres, comparing anticipated layer heights to determine optimal photoresist thicknesses desired..



Using the appropriate thickness of photoresist, patterning can them be accomplished and used with the deposition vessels above to attempt to control nanosphere placement.

# 3.RESULTS

## 3.1 Drain-Coating Deposition

The evolution of the deposition vessel described in the previous section was primarily driven by the literature, but some design choices were made based on results obtained during testing. For example, Wang et al predicts that the optimal angle of the substrate to the liquid surface is a function of the size of the spheres as well as the fluid properties of the carrier liquid, which affects the geometry of the meniscus of the edge of the fluid. Using that relationship, the first vessel tested optimal angle theory and found it to be between 15° to 25°, so for the rest of the vessels this angle was set to 20°. These values however are particular to this set of materials and my need to be altered for other size spheres, particle composition, carrier fluid mechanics, etc.

The first vessel shown in Figure 2 resulted in typically two different deposition trends. Either very little particles were patterned or an excess of particles (resulting in multiple layers of self-assembled planes) resulted. This variation appeared to be the combination of two sources of variability: first was the ratio of surface vs. sub-surface nanospheres and second was the rate of carrier liquid removal. Through trial and error it was determined that the best monolayers were produced from a vessel in which most of the nanospheres were sub-surface and drained at a very slow rate (typically 0.1 – 0.3 mL/min). The best multilayers on the other hand appeared to be formed when a majority of the nanospheres were floating, but drainage occurred at a faster rate (typically 0.75 mL/min). These results led to the second vessel (shown in Figure 3) as producing the best results.

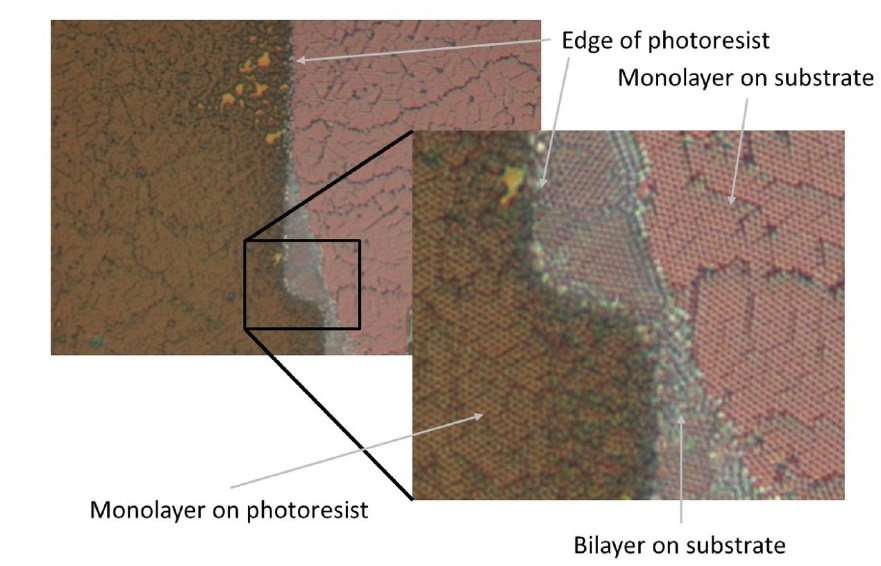
The Langmuir trough design did show promise in condensing surface particles. To transfer these patterned layers to a substrate effectively requires much more precise control of the drain rate and minimal disruptions during the process. As will be shown in the next section where pattering is attempted, sub-surface nanospheres proved to be more effective and as such, the second vessel design proved to be the most successful overall.

For this vessel, the glass slide was placed first, and the deionized water filled to a level above the carriers, below the bottom edge of the glass slides. The samples were then loaded onto each holder, and the water level carefully increased until it was even with the bottom edge of the glass slides, but no higher (to keep the glass surface dry for now). The nanosphere solution was prepared as described in Section 2, loaded into a pipette, and set aside. Ethanol was then used to wet the slides and once the flow of ethanol onto the water surface stabilized, the ethanol drip was replaced with the nanosphere solution, which was slowly applied to the slide. Once loaded and the nanospheres were at rest, drainage began and was allowed to continue at least until the liquid had dropped beneath the samples at the appropriate drain rate described above. Each of these steps improved the ratio of monolayer nanoparticles in uniform formation on the substrate, with the best coverage accomplished at around 80% surface area, with usable areas well over 1-10 mm2.

## 3.2 Patterning

Patterning was attempted with nanosphere monolayers formed on the surface of the carrier fluid as well as sub-surface deposition methods. For the pre-patterned surface monolayers, refer to Figure 8. While the basic structure of the monolayer remained intact after its transfer to the patterned substrate, several small breaks occurred throughout. Additionally, the edge of the photoresist tended to cause disruptions in the monolayer. In some cases this was simply a gap, but as shown in Figure 8 this also caused another pattern to occur. In this figure, the right-most region shows the monolayer directly on the substrate and the leftmost layer shows the monolayer on the photoresist. The region in between however is the formation of a bilayer during the nanosphere placement, where a break in the monolayer occurred due to the edge of the photoresist, and the ‘tear’ in the monolayer which occurs approximately half way down the image forms an inverted ‘V’ shaped region of overlap.

Figure 8. Patterning results of depositing pre-assembled surface monolayers onto patterned substrate with photoresist of comparable thickness.



Patterning was also attempted using sub-surface nanoparticle deposition process, allowing them to slowly transfer and self-assemble as the carrier fluid was drained. To accomplish this test, a mask was produced using the 1 μm beam diameter Heidelberg laser lithography system with a test pattern shown in Figure 9, part (A). This pattern was designed to promote specific placement as well as orientation while testing the optimal size of channels and features. The thickness of the photoresist pattern with this mask was roughly 700nm. A single deposition run was performed on these samples, which resulted in coverage of approximately 5 to 10% of the exposed substrate, and virtually no particles being deposited on the photoresist. One of the several areas which was patterned is shown in Figure 9, part (B) as well as magnified in Figure 10.

Figure 9. Patterning results of sub-surface 500 nm nanospheres on test pattern. Full test pattern on the left (A) and square indicates section which was imaged on the right (B). The thickness of the photoresist was approximately 700 nm, resulting in monolayer depositions in the patterned channels.

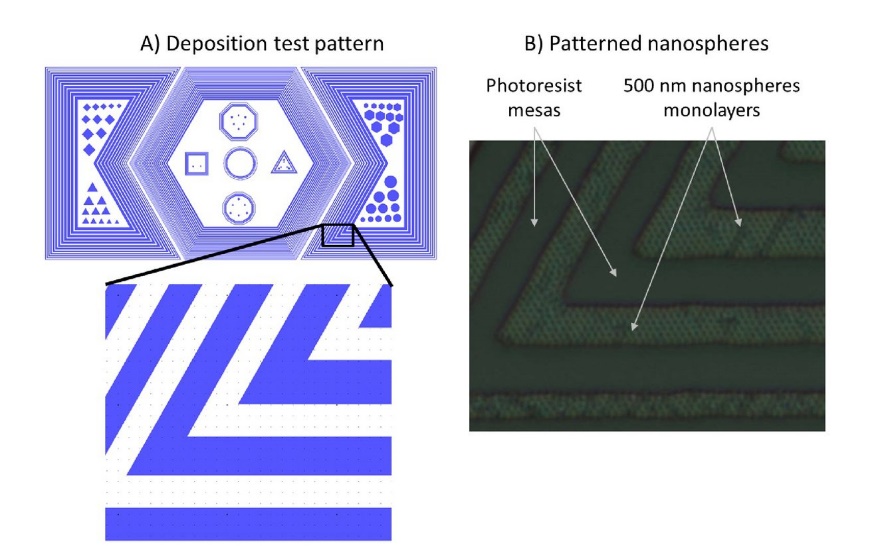
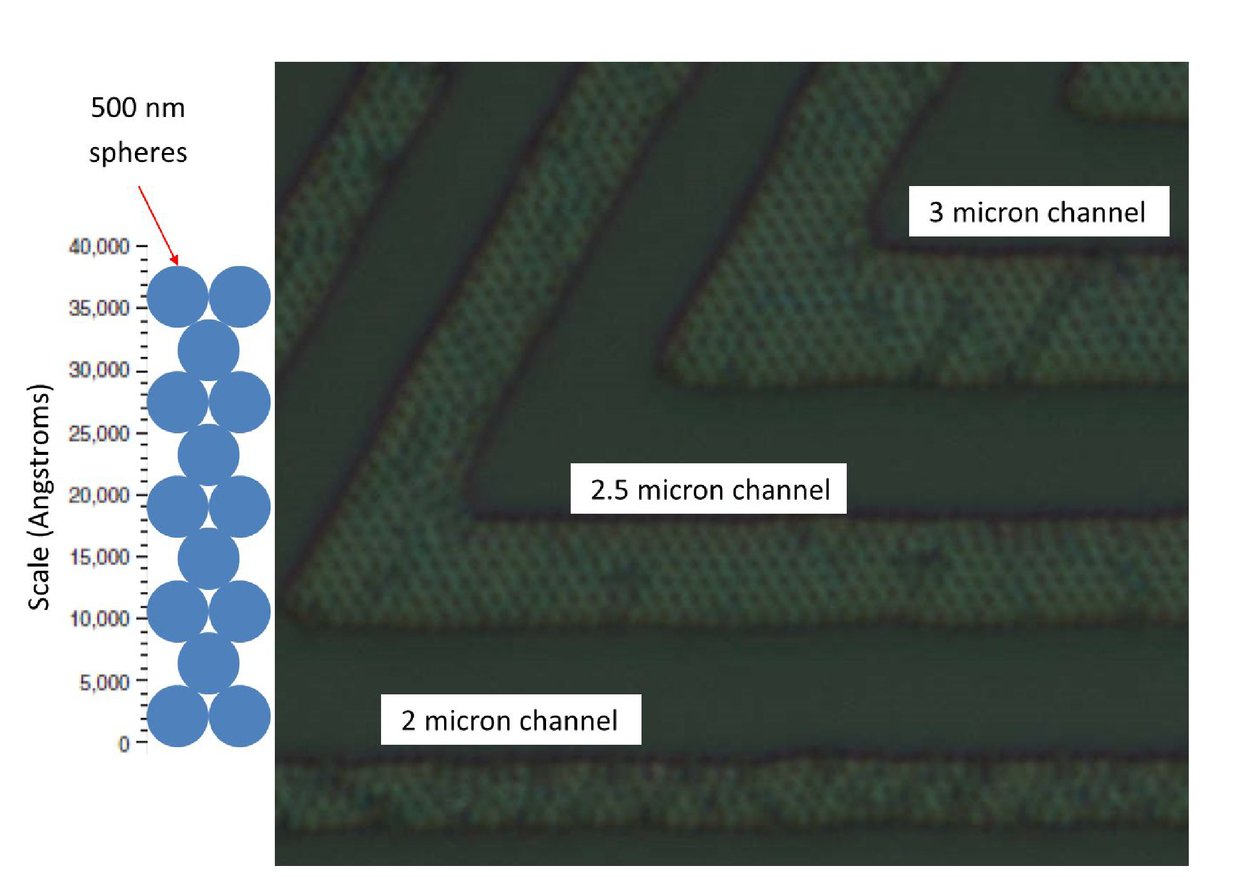


Figure 10. Magnified image of captured nanospheres in channels of photoresist of ∼700nm thickness, showing pattern irregularity varying with channel width. For the 500 nm diameter spheres used, the bottom channel is oversized for four rows of spheres, but not enough space for five resulting in irregularities. For the 2.5 micron channel however, this is just enough space to accommodate six rows of spheres and in the 3 micron channel, seven rows will fit.



A larger magnification of the captured nanospheres is shown in Figure 10. On the left side of this figure, we have an illustration of 500nm spheres next to a scale to compare the expected stacking vs. observed results, which also indicates size requirements for horizontal dimensions. In the bottom, 2μm wide channel (20,000 Angstroms on the scale shown) we can see that it is not enough space to accommodate five full rows. However, the extra space present with only four rows will lead to patterning with a great deal of irregularity. In the 2.5 μm and 3μm channels however, these are just enough space to fit six and seven rows of nanospheres respectively. Note that test pattern contained a number of channels over a wide range of widths. All the channels which were less than 2μm had few nanospheres present, and once the channel width reached around 5μm it behaved more like an open wafer than a channel.

# 4.CONCLUSIONS

Self-assembled nanosphere layers were successfully produced using vessels build from commercially available 3-D printing technology. The materials used in these tests consisted of 500nm polystyrene spheres suspended in an ethanol/Triton-X solution, and deionized water as a carrier. The substrates used were silicon patterned with 1800 series photoresist. The optimal angle between the substrate and liquid surface was between 15 to 25 degrees. The placement of the nanospheres on the surface of the carrier as well as the rate at which the liquid was drained seemed to produce a trend in the type of deposition which occurred. If a large number of floating nanospheres and a relatively fast drain rate were used, this resulted in more multilayers forming. If the floating spheres formed uniform planes and the transfer was with minimal disturbances, then the multilayers tended to be well formed as well. However, if the nanospheres were primarily sub-phase and not floating, then patterning would only occur at a much slower drain rate and typically resulted in monolayers. The addition of a Langmuir trough design did concentrate the surface concentration but requires more fine control of drain rate to truly evaluate its potential benefits.

Using these kinds of deposition in conjunction with classical photoresist patterning techniques produced patterned nanospheres within the patterned areas of photoresist. In the case of transferring pre-formed monolayers from the carrier liquid surface to the substrate containing patterned photoresist, the edges of photoresist tended to break apart the layers and either cause gaps in the patterning, or overlap resulting in both bilayers and monolayers within the patterned regions. Using sub-phased nanospheres during a slow draining process however, patterning did occur within open areas of photoresist. For 500 nm polystyrene nanospheres, channels of 1800 series photoresist which were roughly 700nm thick we able to control the patterns formed in channels between 2 – 5 microns. Most channels smaller than 2 microns contained a negligible number of nanospheres, while areas greater than 5 microns simply behaved more as an open wafer. Ideal patterning occurred between 2.5-3 microns and particularly in channels which were sized specifically to accommodate the final expected pattern size without a great deal of excess space. Finally, patterns which contained enough space for more rows tend to contain fewer irregularities as the overall structure is better able to accommodate any error in sphere size or less than perfect walls formed in the photoresist and adjust accordingly.

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