UNLOCKING SINGLE MOLECULE DETECTION SENSITIVITIES IN 
SURFACE-ENHANCED RAMAN SPECTROSCOPY

BY

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THESIS

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Single molecule detection sensitivities in surface-enhanced Raman spectroscopy require uniform fabrication of sub-5nm gaps between plasmonic nanoparticles over large areas. For this purpose, researchers have employed ultra-precise fabrication techniques like electron-beam lithography that offer very high resolution, but suffer from low throughput. This thesis proposes a novel solution that combines parallel fabrication techniques of nanosphere lithography and Langmuir-Blodgett assembly with the ability to tune interparticle gaps on stretchable polydimethylsiloxane substrates to fabricate sub-5nm gap bowtie arrays. Toward that end, centimeter-scale nanosphere assembly with large grain sizes of 150μm is demonstrated for hydrophilic silicon substrates. The resulting hexagonally symmetric gold bowtie arrays present three different bowtie motifs that are characterized by 0°, <60° and 60° differences between the grain orientation direction and the evaporation direction. Subsequently, a new polydimethylsiloxane (PDMS) fabrication recipe is developed for making large area stretchable substrates and a hydrophobic nanosphere assembly process results in assembled colloidal mask layers on PDMS substrates equivalent in quality to the colloidal mask layers on silicon substrates. Finally, linear tuning of bowtie gaps with modulation of strain in underlying PDMS substrates is proved.
To my family and friends
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CHAPTER 1

INTRODUCTION

Raman spectroscopy is a molecular fingerprint technique used to observe the vibrational, rotational, and other low-frequency modes in a material [1]. In this technique, a monochromatic light source, like a laser, illuminates the material of study, which excites the constituent molecules to higher vibrational and rotational states. The excited molecules return to a lower state by emitting photons that are shifted in energy with respect to the source photons, and generating phonons that are characteristic to the chemical bonds in the molecule. These energy shifts relay sufficient information for precise characterization of the molecular structure. However, since the emitted (inelastically scattered) light is captured by filtering out the dominant elastically scattered light, the resulting Raman signals usually have low intensities and low signal-to-noise ratios. Surface enhanced Raman spectroscopy (SERS) solves this bottleneck by employing localized surface plasmon resonances (LSPRs) in metal nanoparticles (Figure 1.1) to enhance the scattered light from the molecules [2]. LSPRs are coherent conduction electron oscillations excited by the interaction of electromagnetic radiation with sub-diffraction length nanoparticles having negative real and small positive imaginary dielectric constants [3, 4]. These plasmon resonances have been shown to demonstrate incredible properties of high quantum efficiency light absorption [5], sub-diffraction limit confinement of energy [6], near-perfect forward scattering anisotropy [7] and extraordinary electric field enhancements [8]. Naturally, plasmonic nanostructures are very attractive toward nanophotonic applications requiring a boost in light absorption or scattering.

Even though the SERS phenomenon was first discovered in the 1970s [9], reliable fabrication of large-area uniform high-enhancement substrates remains an unsolved challenge [10, 11]. Ultra-high SERS enhancements have been unlocked by fabrication of sub-10nm gap nanoparticles through chemical synthesis methods [12, 13] and lithographic patterning using electron-beam lithography (EBL) [8, 14–16]. However, chemically fabricated systems suffer from lack of re-
Figure 1.1: Localized surface plasmon resonance [3]

 producibility and small surface areas of active plasmonic sites, and EBL suffers from high costs and low throughputs. Nanosphere lithography (NSL) is an inexpensive, easy to implement, inherently parallel, high throughput, materials general nanofabrication technique that is capable of producing an unexpectedly large variety of structural shapes and well-ordered nanoparticle arrays [17]. The lithography technique has been applied to fabricate hexagonally symmetric arrays of triangular nanoparticles with optimized enhancement levels approaching $10^9$ [18] and bowties with gaps from 4nm to 25nm [17]. However, NSL suffers from large process variabilities in the sub-10nm regime that limit fabrication of uniform high-enhancement plasmonic arrays. We propose a novel process that fabricates large-area arrays of sub-40nm gap bowties using NSL on polydimethylsiloxane (PDMS) substrates and subsequently employs substrate strains to linearly tune bowtie gaps to sub-5nm regime with high fidelity. In this thesis, we detail the NSL fabrication process and characterize the resulting bowtie arrays on silicon and PDMS substrates. Finally, the ability to linearly tune bowtie gaps on strained PDMS substrates is demonstrated.

1.1 Unlocking Single Molecule Detection Sensitivities

Metal nanoparticle plasmon resonances are dependent on the shape, size, spacing, orientation, and refractive index of the particles, as well as the refractive index of the environment [17, 19]. Researchers have shown that low aspect ratio particles, i.e., spherical particles, demonstrate LSPR peaks in the green part of the visible spectrum (Figure 1.2) and electric field enhancements $\sim$200. Higher aspect ratio particles, i.e., triangle particles, demonstrate a red-shifted LSPR peak (Figure 1.2) and enhanced enhancement factors ($\sim$3500) due to free
electron metal response at higher wavelengths and the lightning rod effect [20]. Optimizing the arrangement of particles in an array unlocks an additional degree of SERS enhancement due to coupling between the near-field interactions and far-field diffractive modes [11, 21]. Using these design principles, Gopinath et al. have shown spatially averaged enhancement levels of $10^7$ in EBL fabricated aperiodic triangular nanoparticle arrays [11] and Zhang et al. have shown enhancement levels of $7.1 \times 10^9$ in NSL fabricated hexagonally symmetric triangular nanoparticle arrays [18]. Higher enhancement levels can be achieved by replacing monomer particles with dimers and trimers of particles, with a correlated increase in SERS enhancement levels and reduction in nanoparticle separations down to 1nm (Figure 1.3) [14, 15]. Hatab et al. demonstrated this principle by obtaining enhancement levels approaching $10^{12}$ in periodic arrays of 8nm gap bowties fabricated by EBL [15]. We expect single molecule sensitivities (enhancement levels of $10^{12} - 10^{14}$) to be unlocked by deterministic fabrication of hexagonally symmetric arrays of sub-5nm gap bowties.
1.2 Angle-Resolved Nanosphere Lithography

The NSL process starts with an assembly of a two-dimensional colloidal sphere mask layer on the target substrate. Subsequently, metal is evaporated through the mask layer by thermal evaporation or e-beam evaporation. The resultant metal pattern of hexagonally symmetric bowtie arrays (Figure 1.4) can be obtained by dissolving the spheres using ultrasonication in a polar solvent.

We can calculate the perpendicular length of a bowtie triangle \( a \) and the interparticle distance \( d_{it} \) as a function of the sphere diameter \( D \) as [17],

\[
a = 1.5 \times (\sqrt{3} - 1 - \frac{1}{\sqrt{3}}) \times D, \tag{1.1}
\]

\[
d_{it} = \frac{D}{\sqrt{3}}. \tag{1.2}
\]

Figure 1.5 graphs the NSL parameters as a function of the sphere diameter. It is observed that both parameters cannot be optimized simultaneously, i.e., choosing an optimal triangle length of 120nm [8] results in a large interparticle distance of 289nm. Since the resulting interparticle distances are much greater than the electric field propagation length for a triangular nanoparticle, no near-field coupling (a requirement for ultra-high electric fields) is expected between the bowtie triangles. Therefore, traditional NSL cannot be used for our experiments. Figure 1.6 shows a SEM measurement of the large interparticle distances for 1μm diameter spheres.
Figure 1.4: Hexagonally symmetric bowtie arrays

Figure 1.5: Bowtie triangle length and interparticle distance as a function of sphere diameter
Angle-resolved nanosphere lithography (AR-NSL) is a simple variant to the conventional NSL technique that employs metal evaporation at small angles off the normal direction to the substrate [22]. This allows the user to flexibly optimize the bowtie gap for appropriately sized triangle lengths. Figures 1.7a and 1.7b showcase the flexibility of AR-NSL as compared to NSL. For a single evaporation normal to the substrate, we obtain a traditional hexagonally symmetric bowtie pattern with large interparticle distance. However, if two evaporations are performed at \(\pm 15\) degrees from normal, the bowtie gap can be reduced to sub-50nm lengths along the evaporation direction. Note that the bowties triangles no longer remain equilateral. The perpendicular length along the evaporation direction changes by \(\sim\)5nm, however, the remaining two perpendicular lengths change by \(\sim\)50nm [22].
Figure 1.7: (a) NSL simulation output; (b) AR-NSL simulation output at ±15°; simulations performed in Cinema4D

1.3 Langmuir-Blodgett Assembly

Langmuir-Blodgett assembly (LBA) is a liquid-gas interface self-assembly technique for preparation of centimeter-scale colloidal mask layers on target substrates [23–26]. It offers the benefits of easy implementation, small processing time and large defect-free grains on the order of 100μm with a high level of hexagonal symmetry. This process, as detailed in Figure 1.8, starts with the preparation of the application solution, i.e., 10% nanosphere solution in water is mixed with equal volume of ethanol. Ethanol reduces the specific density of the mixture, thus enabling optimal spreading on the water-air interface. Upon application, the spheres tend to form disordered chains that can subsequently be assembled into large ordered grains by the addition of a surfactant solution. Researchers have shown that small volumes of 2% sodium dodecyl sulfate (SDS) solution lead to optimal grain packing [27], which can be easily monitored by visible bright diffraction patterns off the grains. Finally, the resulting assembled layer is gently dropped on to the submerged target substrate by removing the water from the bath. The target substrate is kept at a small angle (10°) off the horizontal to allow for a linear drying front and prevent stress accumulation in the colloidal crystal layer [26, 28]. After the process, the substrates are allowed to dry in air.
The LBA assembly setup is dictated by the hydrophilicity of the target wafer as shown in Figure 1.9. Hydrophilic substrates, like glass or silicon substrates, possess small water contact angles and thus allow spheres to be picked up by withdrawing the substrate out. On the other hand, hydrophobic substrates, like polymer substrates, have to pick up spheres by pushing the substrate into the water.
CHAPTER 2

BOWTIE ARRAYS ON SILICON SUBSTRATES

Silicon wafers are chosen as test substrates for developing the large-area gold bowtie array fabrication recipe. They offer the benefits of easy availability, extremely flat surfaces and well-understood chemistries. We employ the use of silicon wafers with <100> orientation. The wafers were cut to size using a diamond scribe, and cleaned with ultrasonication in solvents and 250W oxygen plasma for 10 minutes each. Alternative cleaning processes like RCA SC-1 can also be used.

The Langmuir-Blodgett assembly recipe detailed as follows has been adapted from past literature [23–26]. Nearly monodisperse polystyrene spheres of diameters 1μm are purchased in 10% wt. solution from Sigma Aldrich. Even though the target sphere diameter for optimally sized bowties is 500nm, we choose bigger spheres for ease of fabrication and characterization. The application solution of equal volumes of 10% polystyrene sphere solution and ethanol is prepared (Figure 2.1a). Subsequently, we construct the assembly setup, which consists of the assembly trough containing Milli-Q water and the submerged target wafer. The size of the assembly trough is dictated by the intended colloidal mask layer area. Hence, we employ the use of 4” wafer petri dishes for our assemblies. The target wafer is kept at a small angle (5-10°) off the horizontal. Our experiments have achieved this in two ways. The first method uses a home-built ramp setup (Figure 2.1b) made from a 0.125” thick aluminum piece and a wedging 6-32 screw. The ramp angle can be adjusted by changing the length of the screw underneath the aluminum block. Further, the top surface of the ramp is filed to induce a small notch to keep the silicon substrates from slipping. The benefits of this method are controlled wafer placement that is ideal for smaller wafers, precise incline angles and elevation of the wafer off the base of the trough for efficient drying. However, this method is tough to scale up for large wafer sizes and requires a better solution for keeping wafers adhered to the ramp. Therefore, for large-area assemblies, we employ a simpler second method in which we use a glass slide
spacer block to wedge the assembly trough, as shown in Figure 2.1c. A smaller
glass slide spacer is used to elevate the wafers off the base of the trough. In this
method, the assembly area is only restricted by the trough size and the incline
angle.

Once the setup is constructed, 40-50µl of the application solution is slowly
added to the water surface. The amount of solution added depends on the in-
tended colloidal mask layer area. Assuming a two-dimensional colloidal mask
area of 1cm², an effective sphere area (A) is

\[
A = \text{Mask layer area } \times \text{Circle packing density},
\]

\[
A = 1\text{cm}^2 \times 0.9069 = 0.9069\text{cm}^2.
\]  

The number of 1µm spheres (N) covering the effective sphere area are

\[
N = \frac{A}{\text{Crosssectional area of sphere}},
\]

\[
N = \frac{0.9069\text{cm}^2}{\pi \times (0.5 \times 10^{-4})^2} = 1.15 \times 10^8.
\]  

Using 5% concentration of the application solution and a 1.04 g/cm³ density for
polystyrene, the volume of the application solution (V) required for N spheres is

\[
V = \frac{N \times \text{Volume of one sphere} \times \text{Polystyrene density}}{\text{Solution concentration}}.
\]
Figure 2.2: (a) Unordered sphere layer on water surface; (b) Ordered sphere layer on water surface; (c) Large-scale assembly on a silicon wafer

Therefore, 1.25μl is required for a colloidal mask layer of 1cm². For 40-50μl, we expect a mask layer of 32-40cm². Once the spheres have been added to the water surface, we observe the formation of an unordered colloidal mask layer as seen in Figure 2.2a. Subsequently, 4μl of 2% SDS solution is pipetted to self-assemble the spheres into ordered large grains, as evidenced from the bright diffraction patterns in Figure 2.2b. Scanning electron microscopy (SEM) proves that the colorful diffracting layer is a monolayer, while the small white parts are the multiple layers sitting on top of the monolayer. Finally, a syringe pump is used to slowly remove water from the trough and the spheres gently assemble on the silicon substrate. Figure 2.2c shows the silicon substrate after drying in air for 24 hours. We observe that the diffracting colloidal layer on the water surface is almost exactly transferred onto the silicon substrate, thus successfully achieving centimeter scale assembly.
Following the assembly of the colloidal mask layer, we evaporate gold onto our substrates using a Denton Vacuum DV-502A thermal evaporator (Figure 2.3a). We use gold because of its excellent plasmonic properties and inertness to oxidation in air. Further, adhesion layers are found to be non-essential in our experiments. Figure 2.3b details our setup, which contains two electrodes that are loaded with gold flake packed tungsten boats, and, a box frame for placement of the inverted substrate and the thickness monitor crystal above the metal sources. Thermal evaporation allows easy control of the relative angles between the substrate and the sources, which are kept at $\pm 15^\circ$. All evaporations are performed at $5 \times 10^{-6}$ torr pressures.
Scanning electron microscopy (SEM) is employed to characterize the colloidal mask layer at turbo pressures, 10kV accelerating voltage and 7mm working distance. Figure 2.4 shows large-area scans of the colloidal mask grain layout. We observe multiple grains with sizes >100μm and the biggest grains on the order of 150μm, which are competitive with results shown in past literature. These grains can be further optimized by using ultrasonic impulses to achieve the Ostwald ripening effect [29]. Additionally, we observe crystal defects that are assigned as grain boundaries, line defects, vacancy defects, stress defects [28] and multiple layers. These defects have been labeled in Figure 2.5. A zoomed-in scan, Figure 2.6, showcases the hexagonal symmetry pattern of the self-assembled nanospheres with the voids outlining the single evaporation bowtie pattern. We observe an additional defect of nanosphere size disparity in this image.
Figure 2.5: Crystal defects

Figure 2.6: Hexagonal symmetry of self-assembled nanospheres
Colloidal spheres are subsequently removed by 3 minute ultrasonication in ethanol [17]. After drying, SEM scans characterize the bowtie layout in the substrate. We observe three different bowtie motifs (Figure 2.7) that are fabricated based on the difference between the grain orientation direction and the evaporation direction. This difference can be restricted to 60$^\circ$ due to the hexagonal symmetry of the bowtie arrays. Therefore, nano-overlap bowties are a result of aligned evaporation, the misaligned bowties are a result of $<$60$^\circ$ difference and the parallel bowties are a result of 60$^\circ$ difference. Furthermore, large-sized grains (>100$\mu$m) are abundantly found for all three motifs. Figure 2.8 shows one such grain for nano-overlap bowties with excellent hexagonal symmetry. We see that the defects in the evaporation pattern, as labeled in Figure 2.9, can be attributed to the defects in the colloidal mask layer.

Figure 2.7: (a) Aligned motif; (b) Misaligned motif; (c) Parallel motif
Figure 2.8: Large nano-overlap bowtie array

Figure 2.9: Evaporation pattern defects
Polydimethylsiloxane (PDMS) is a polymeric organosilicon compound that is fabricated by a crosslinking reaction between a siloxane-based base and a platinum-based curing agent [30]. Cured PDMS substrates are frequently employed in soft lithography applications because they are cheap to make, optically transparent, non-reactive, flexible and stretchable up to 160% strains [31]. The fabrication recipe for our PDMS substrates is detailed as follows [30, 32]. As a first step, vigorously mix Dow Corning 184 Sylgard PDMS base and cure in a ratio of 10:1 respectively. Subsequently, construct the mold for curing the PDMS mixture, as shown in Figure 3.1a. It consists of a 3" × 2" glass slide that serves as the flat curing surface and an aluminum pipe that provides enclosure for the viscoelastic PDMS mixture. Special attention is given to not include plastic components in our setup for the purpose of using higher curing temperatures. Clean the glass slide by solvent ultrasonication and UV-ozone plasma for 10mins each. After the mold is constructed, pour the PDMS mixture inside the mold and degas for 60mins in a vacuum oven. In order to maximize the stretchability of our substrates, we aim to keep our substrate thicknesses to 2-3mm [33]. Following removal, partially cure PDMS at 90°C for 15mins, which changes its form from a viscoelastic liquid to an elastic solid. At this point, the aluminum pipe can be removed for easier substrate extraction at the end of the fabrication process. Finally, cure the setup at 90°C for an additional 45mins. Once the PDMS mixture has cured, the setup is put in a freezer for 5mins. This allows easy extraction of large-area defect-free PDMS substrates with tweezers (Figure 3.1b).
We pursue fabrication of the nanosphere colloidal mask layer on our PDMS substrates three different ways, namely, transfer printing from silicon substrates to PDMS substrates, direct assembly on hydrophilic PDMS substrates and direct assembly on hydrophobic PDMS substrates. Here, we explore these methods in more detail. Transfer printing enables heterogeneous material integration from different substrates into a single device using kinetically controlled adhesion to elastomeric stamps [34]. Many studies toward tunable plasmonics have employed transfer printing of colloidal crystals from gold or silicon substrates to PDMS substrates [35–37]. However, the efficiency of the transfer process depends on achieving conformal contact of the stamp with the sphere layer, control of the kinetics and the quality of the stamp. In our experiments, we found that direct assembly of colloidal crystal on PDMS substrates led to larger grain sizes and fewer defects than transfer printing from silicon substrates. Figures 3.2a and 3.2b show a silicon substrate and a PDMS stamp, respectively, that are used for transfer printing with an applied pressure of 23.19kPa. The resulting partially transferred colloidal mask layer is shown in Figure 3.3.
The silicon LBA process developed in Chapter 2 is a materials-independent assembly technique that can be ported for hydrophilic PDMS substrates. As discussed in Section 1.3, the requirement for substrate hydrophilicity stems from the small contact angles made by water on submerged hydrophilic substrates, thus allowing easy transfer of colloidal sphere layers. This claim is tested by developing a control experiment where both hydrophilic and hydrophobic PDMS samples are placed on glass slides inside the assembly trough (Figure 3.4a). It is important to note that PDMS is intrinsically a hydrophobic polymer (Fig-
ure 3.4b), but can be made hydrophilic temporarily by treatment with oxygen plasma at 150W for 1min (Figure 3.4c) [38]. Performing the control experiment, we see selective assembly of nanospheres on the hydrophilic PDMS substrate (Figures 3.4d) and the glass slides, but small assembly on the hydrophobic PDMS substrate (Figure 3.4e).

Figure 3.4: (a) Control experiment setup; (b) Hydrophobic PDMS; (c) Hydrophilic PDMS; (d) Hydrophilic PDMS with centimeter-scale coverage; (e) Hydrophobic PDMS with small coverage
Following a gold evaporation step, we characterize the assembled colloidal mask layer on the hydrophilic PDMS substrate using SEM. Scans are taken at turbo pressures, 10kV accelerating voltage and 6mm working distance, and gold is evaporated using the silicon AR-NSL evaporation setup. In Figure 3.5, we show a large-area scan of a nanosphere island on a hydrophilic PDMS substrate. It is seen that the average grain size is limited to 20-30μm by the high density of substrate defect lines (Figure 3.6). We believe that the substrate defect lines originate due to the large force required to separate the PDMS substrate and the glass slide following the oxygen plasma step. As noted in past literature [39], oxygen plasma leads to oxidation of the surface methyl groups in PDMS, which subsequently results in strong covalent bonding between the PDMS substrate and the glass slide. Additionally, after the removal of the colloidal mask layer with ethanol [40], we observe same bowtie motifs on either side of the defect lines (Figure 3.7). Hence, the self-assembled grains on water have larger sizes than the resulting grains on the hydrophilic PDMS substrate.

Figure 3.5: Large monolayer assembly
Figure 3.6: Substrate defects

Figure 3.7: Same bowtie motif on either side of defect; SEM scan taken at 1torr water vapor pressure, 20kV accelerating voltage and 7mm working distance
The hydrophobic LBA process, a variant of the hydrophilic LBA process, extends the capabilities of the original technique towards preparation of large-scale colloidal mask layers directly on the target hydrophobic substrates, thus alleviating the need for additional fabrication steps like substrate oxidation or transfer printing. As discussed above, employing hydrophobic substrates in the hydrophilic LBA setup results in a very inefficient assembly due to the harsh contact angles made by water on the submerged hydrophobic substrates. Therefore, as shown in Figure 1.9, the hydrophobic substrate needs to be placed above the water surface. This can be achieved by employing the use of a 4” plastic petri dish cover for our assembly trough and adhering the PDMS substrate to the inside surface of the cover. Figure 3.8 details this setup. A 2” plastic petri dish cover is used to induce a small angle of 5-10° in our PDMS substrates. Additionally, holes are made in the 4” petri dish cover to provide feedthrough to the syringe pump. It is important to note that the entire setup is constructed from hydrophobic components to avoid complex forces on the water surface.

Once the setup has been constructed, we prepare the application solution of equal volumes of the 10% polystyrene sphere solution and ethanol. Subsequently, we fill the assembly jar halfway with Milli-Q water and slowly add the required amount of the application solution to the water surface. As discussed in Chapter 2, the required amount of the application solution can be calculated based on the desired area of the final colloidal mask layer. At this point, we observe an unordered sphere layer forming on the water surface, which can be bunched together to form an ordered layer by adding 4μl of 2% SDS solution. Finally, we add
more water to the trough and the sphere layer gently assembles on the PDMS substrate. After the assembly, the substrates are dried in air for 24 hours. We employ SEM to characterize the resulting colloidal mask layer following gold evaporation. Figure 3.9 shows a large-area SEM scan taken at turbo pressures, 10kV accelerating voltage and 7mm working distance. It is seen that the nanosphere grains on hydrophobic PDMS are similar in size to the nanosphere grains assembled on silicon. Further, no surface defect lines are observed underneath the grains. Therefore, direct assembly on hydrophobic PDMS substrates provides us with the best colloidal mask layers.

Figure 3.9: Large monolayer assembly; courtesy of Eric Wynne
3.1 Strain Tuning Bowtie Gaps

As a final study in this thesis, we test the capability to linearly tune gaps between bowtie triangles by modulating the strains in the underlying PDMS substrates. This principle, even though proved for micron-sized spheres [13], has not been explicitly proven down to the nano-scale or demonstrated for complex geometries like bowties. For this purpose, we study the change in the morphology of a bowtie with tensile strains up to 15%. Future experiments will repeat this study with compressive strains up to 15%. We employ a home-built setup to stretch our PDMS substrates as shown in Figure 3.10. The setup consists of two aluminum blocks sitting on rails, and, a 10-32 screw that is threaded through one of the blocks and pushing against the other block. Hence, we induce tensile strain in our PDMS substrates by adhering them to the aluminum blocks and subsequently increasing the spacing between the blocks by clockwise rotation of the 10-32 screw. We have found that commercially available super glue provides fast and reversible bonds between PDMS and aluminum, which support reliable symmetric strains in our substrates.

![Home-built stretching setup](image)

**Figure 3.10: Home-built stretching setup**

In our setup, one turn of the 10-32 screw increases the substrate length by
the pitch \( (p) \) of the 10-32 screw. Therefore, the length change \( (\Delta l) \) in the PDMS substrate per turn of the 10-32 screw \([41]\) is

\[
\Delta l = p = 0.7938\text{mm.} \tag{3.1}
\]

Assuming an original substrate length \( (l) \) of 1.1cm, the strain induced \( (s) \) per turn of the 10-32 screw is

\[
s = \frac{\Delta l}{l} \times 100 = \frac{0.7938\text{mm}}{1.1\text{cm}} \times 100 = 7.21\%. \tag{3.2}
\]

![Figure 3.11: Bowtie schematic](image)

Further, assuming 1\( \mu \)m diameter \( (D_s) \) spheres are used to fabricate 35nm gap \( (g) \) bowties (Figure 3.11) on the PDMS substrate, the resultant length \( (a) \) of AR-NSL triangles \([17, 22]\) is

\[
a = 1.5 \times (\sqrt{3} - 1 - \frac{1}{\sqrt{3}}) \times D_s \text{ - Adjustment for ARNSL,} \tag{3.3}
\]
Finally, assuming the anchors for both triangles are half-way up the perpendicular triangle lengths, the separation \(d\) between the anchors is

\[
d = \frac{a}{2} + \frac{a}{2} + g,
\]

\[d = \frac{222.05}{2} + \frac{222.05}{2} + 35 = 257.05\text{nm}.
\]

Due to the strain induced by the 10-32 screw, the new separation \(d'\) becomes

\[
d' = d \times \frac{s}{100} = 275.58\text{nm},
\]

which gives a new gap \(g'\) of

\[
g' = d' - d + g = 275.58 - 257.05 + 35 = 53.53\text{nm}.
\]

Therefore, one turn of the 10-32 screw leads to an increase in the bowtie gap from 35nm to 53.53nm. Similarly, the expected gap value for two turns of the 10-32 screw is 72.07nm. These results can be verified by measuring the inter-triangle gap from high-magnification SEM scans of an aligned gold bowtie on a strained PDMS substrate. SEM images taken at 1torr water vapor pressure, 10kV accelerating voltage, 5.8mm working distance, and, substrate strains of 0%, 7.21% and 14.42% are shown in Figure 3.12. We calculate the displacement of the target bowtie with change in substrate strain using a python script, which has been detailed in appendix A. It is seen that the bowtie gap stretches along the axis of the bowtie with little distortion or delamination of the bowtie triangles. Additionally, the bowtie gaps show excellent linear correlation with the PDMS substrate strain over a gap increase of 100% (Figure 3.13). We expect the same linear correlation to extend from the gap range of 35nm down to sub-10nm.
Figure 3.12: Gold bowtie on PDMS substrate strained at (a) 0%, (b) 7.21% and (c) 14.42%
Figure 3.13: Experimental and theoretical strain tuned bowtie gap values
CHAPTER 4

FUTURE WORK

In this thesis, we developed a novel process that combines parallel fabrication techniques of angle-resolved nanosphere lithography and Langmuir-Blodgett assembly with the ability to tune interparticle gaps on stretchable PDMS substrates. Toward that end, we tested the LBA process for 1µm polystyrene spheres on hydrophilic silicon substrates and observed centimeter-scale nanosphere assembly with multiple grains of sizes >100µm and biggest grains on the order of 150µm. Subsequently, we evaporated gold at ±15° to achieve sub-50nm gap hexagonally symmetric bowtie arrays and observed three different bowtie motifs, namely, aligned motif, misaligned motif and parallel motif, which were characterized by 0°, <60° and 60° differences between the grain orientation direction and the evaporation direction.

We developed a new fabrication recipe for large-area (2.5” × 1.5”) 1-3mm thick PDMS substrates. The recipe featured removal of the aluminum pipe enclosure after the PDMS substrates were partially cured to facilitate easy substrate extraction at the end of the fabrication process. Subsequently, we evaluated colloidal mask layer fabrication on PDMS substrates for three methods, namely, transfer printing from silicon substrates, direct assembly on hydrophilic PDMS substrates and direct assembly on hydrophobic PDMS substrates. It was seen that direct assembly on hydrophobic PDMS substrates demonstrated the best grain sizes and quality, which were on par with the silicon LBA results. As a conclusion, we demonstrated linear tuning of bowtie gaps with modulation of strain in the underlying PDMS substrate.

Future work in this project aims to fabricate and study large arrays of sub-5nm gap bowties on strained PDMS substrates. This will be achieved by applying the AR-NSL process on prestrained PDMS substrates to fabricate sub-30nm gap bowtie arrays and relaxing the strain to reduce bowtie gaps down to the sub-10nm regime. High-magnification SEM scans will be used to characterize the efficiency of the gap tuning process and the variance of the bowtie gaps across
an array. The resolution requirements for efficient gap measurements in the sub-5nm regime may demand the use of a conductive graphene underlayer. Finally, Raman spectroscopy will be employed to measure the variance and the average of the plasmonic enhancement factor for the entire array. Further studies will be done to deduce the effect of fabrication process defects on the SERS enhancement factor and explore the viability of large-area high-enhancement substrates.
This script determines the location of the displaced target point \( c' \) from known locations of end points \( a, b, a' \) and \( b' \), as well as original target point \( c \). From points \( a, b \) and \( c \), we determine the original distances of \( ac \) and \( bc \). Assuming there is only displacement of the substrate with no stretching, we can apply quadratic equations for point \( c' \):

\[
(x - x_a)^2 + (y - y_a)^2 = ac^2
\]
\[
(x - x_b)^2 + (y - y_b)^2 = bc^2,
\]

(A.1)
where, points \(c', a'\) and \(b'\) are given by \((x, y), (x_a, y_a)\) and \((x_b, y_b)\) respectively. These equations can be simplified if one of the end points is shifted to the origin. Shifting point \(a\) to origin, the new coordinates (denoted by adding subscript ‘s’) are

\[
\begin{align*}
x_{as} &= 0 \\
y_{as} &= 0 \\
x_{bs} &= x_b - x_a \\
y_{bs} &= y_b - y_a \\
x_s &= x - x_a \\
y_s &= y - y_a,
\end{align*}
\]

and the simplified equations are

\[
\begin{align*}
(x_s)^2 + (y_s)^2 &= ac^2 \\
(x_s - x_{bs})^2 + (y_s - y_{bs})^2 &= bc^2.
\end{align*}
\]

Finally, the results are adjusted for displacement and strain

\[
\begin{align*}
x &= x_a + x_s \times \text{Strain} \times \text{Poisson ratio} \\
y &= y_a + y_s \times \text{Strain},
\end{align*}
\]

where Poisson ratio for PDMS is 0.5 [42]. The python script code is detailed as follows

```python
""" 2016 Sartaj Grewal """
"""Import libraries"""
import numpy as np
import math
import matplotlib.pyplot as plt

"""Known values"""
ac = 10.6256
bc = 10.8838
```
poisson_PDMS = 0.5

print ("Length ac: "), ac
print ("Length bc: "), bc

"""Stretch_length : length of the substrate""
print("Assuming strain is primarily applied in the y direction")
stretch_length = float(input('Enter stretching length in mm: '))
number_turns = float(input('Enter number of screw turns applied: '))

strain = 1 + ((number_turns*0.793)/stretch_length)
poisson_strain = 1 + poisson_PDMS*((number_turns*0.793)/stretch_length)
print ("Calculated Strain: ", strain)

"""Overlap : Substrate length overlapping the aluminum block
xa, ya, xb, yb : Corner Co-ordinates"
overlap = float(input('Enter overlap length: '))
xa = float(input('Enter x-coordinate of point a: '))
ya = float(input('Enter y-coordinate of point a: '))
xb = float(input('Enter x-coordinate of point b: '))
yb = float(input('Enter y-coordinate of point b: '))

tilt = np.arctan((abs(ya - yb))/(abs(xa - xb)))
print ("Tilt in substrate: ", tilt)

"""xas,yas,xbs,ybs : shifted co-ordinates, simplifies the equations"
xas = xa - xa
yas = ya - ya
xbs = xb - xa
ybs = yb - ya
print ("Shifted coordinate a: ", xas, yas)
print ("Shifted coordinate b: ", xbs, ybs)

"""Quadratic equation parameter a,b and c"
a = 4*(xbs**2 + ybs**2)
b = -4*xbs*(xbs**2+ybs**2+ac**2-bc**2)
c = ((xbs**2+ybs**2+ac**2-bc**2)**2) - 4*(ybs**2)*(ac**2)

\[ d = b^2 - 4ac \]

"""Quadratic solutions""
if xbs == 0:
    print("xb - xa = 0, check placement ")

elif ybs == 0:
    xcs = (xbs**2 + ac**2 - bc**2)/(2*xbs)
xc = xa + xcs
ycs = math.sqrt(ac**2 - xcs**2)
yc1 = ya + ycs
yc2 = ya - ycs
print("Linear Equation - 2 solutions (No strain adjustment)")
print("Triangulated point: \( xc, yc1 \) or \( xc, yc2 \)")
plt.plot([xc,xc], [yc1,yc2], 'ro')

elif d < 0:
    print("Quadratic Equation - 0 solutions")

elif d == 0:
    xcs = (-b/(2*a))
xc = xa + xcs
ycs = math.sqrt(ac**2 - xcs**2)
yc1 = ya + ycs
yc2 = ya - ycs
print("Quadratic Equation - 2 solutions")
print("Triangulated point: \( xc, yc1 \) or \( xc, yc2 \)")
plt.plot([xc,xc], [yc1,yc2], 'ro')

else:
    xcs1 = (-b+math.sqrt(d))/(2*a)
    xc1 = xa + xcs1
    xc1_strain = xa + xcs1 * poisson_strain
    xcs2 = (-b-math.sqrt(d))/(2*a)
    xc2 = xa + xcs2
ycs1 = math.sqrt(ac**2 - xcs1**2)
yc11 = (ya + ycs1)
yc12 = (ya - ycs1)
yc12_strain = (ya - (ycs1 - overlap)*strain*np.cos(tilt) - overlap)
ycs2 = math.sqrt(ac**2 - xcs2**2)
yc21 = (ya + ycs2)
yc22 = (ya - ycs2)

print("Quadratic Equation - 4 solutions (disregarding 3)")
print("Solution: ", xc1, yc12)
print("Strain adjusted solution: ", xc1_strain, yc12_strain)
REFERENCES


