Increased Control over Gold Colloid Adsorption on Substrates for Colloid Displacement Lithography

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INCREASED CONTROL OVER GOLD COLLOID ADSORPTION ON SUBSTRATES FOR COLLOID DISPLACEMENT LITHOGRAPHY

A Thesis
Presented to
The Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

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Of the Requirements for the Degree
Master of Science

By
Vara Prasad Reddy Sakampally

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INCREASED CONTROL OVER GOLD COLLOID ADSORPTION ON SUBSTRATES FOR COLLOID DISPLACEMENT LITHOGRAPHY

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ACKNOWLEDGEMENTS

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Finally, I dedicate my thesis to my parents who supported and encouraged me the most during my challenging times here at Western Kentucky University.
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Colloid displacement lithography is proving to be very effective in the designing of nanometer scale electronic devices. Precise control of the structure of matter at the nanometer scale has brought a revolutionary change in science and technology. The use of these nanometer scale devices ranges from the diagnosis of various diseases to cell repair to ultra strong materials.

This research focused on optimizing the conditions for gold colloid particle adsorption for colloid displacement lithography, an expansion on gold colloid particle manipulation techniques using a scanned probe microscope. The system consists of a scrupulously cleaned glass surface that is coated with poly(diallyldimethylammonium chloride) (PDDA) and then with 5- or 10- nm gold colloid particles. The optimum conditions include the use of very low molecular weight PDDA (Avg MW <100,000 g/mol) or low molecular weight PDDA (Avg MW 100,000-200,000 g/mol) with an exposure time to the glass substrate of 120 to 150 minutes. This is then followed by a 24-hour exposure to the colloid solution. An atomic force microscope (AFM) is used to pattern the thus prepared colloid coated slides. In this work a variety of salts are used as potential blocking agents to prevent or modify the colloid adsorption. These include potassium iodide, potassium bromide, potassium chloride, sodium fluoride, sodium...
sulfate, potassium hydrogen phosphate, potassium hydrogen phthalate, and sodium citrate.

In summary, the following were found as a result of this work:

✓ The optimum conditions that lead to efficient patterning are:
  o Low molecular weight PDDA with a coating time of 120 to 150 minutes.
  o Exposure to 5-nm gold colloid for 24 hours
✓ The most interesting potential blocking agents are the phosphate, sulfate and citrate salts, as they show some potential for modifying the adsorption of the gold colloids on the PDDA.
✓ The dispersion of the colloid particles on the PDDA does not change when using the potential blocking agents compared to direct adsorption on the unmodified PDDA layer.
✓ The use of the potential blocking agents reduces the force required to pattern by a factor of 100 to 300.
INTRODUCTION

The art of writing on a plate or stone with a completely smooth surface is known as lithography. Nanolithography is a rapidly evolving field that constantly requires new combinations of techniques and methods to improve the ease of patterning and to assist in designing various electromechanical devices. Analytical chemists prefer simple methods that ease analyses while improving accuracy and specificity. Colloidal lithography has proven to be a good method for designing nanoelectromechanical systems (NEMS), which are extremely small and fast, and have applications ranging from cell repair to ultra strong materials.¹

Colloidal lithography is a lithographic technique where regular patterns can be constructed by self assembly but special techniques are required to construct complex patterns. Colloidal lithography is a very promising technique for the construction of NEMS.

In the early days manipulation of nanoparticles with an atomic force microscope (AFM) was mostly limited to clearing the areas on the surface or to moving particles to sequentially create two dimensional patterns. In their review, Gorman et. al gave much information regarding the uses of an AFM. They said that AFM is not only used to visualize the surfaces at molecular level but also can modify the surfaces at molecular
level.¹ They elaborated on various techniques and their advantages and disadvantages over each other for nanolithography. They explained various methods used for successful patterning. Amro et. al. have given information regarding how to pattern surfaces by using the AFM tip and methods like nanografting and dip pen nanolithography. They suggested a method for lithography by developing a nano pen reader and writer (NPRW).² In their experiments they coated the AFM probe with adsorbate molecules that adsorb onto newly exposed areas created by the AFM tip. They combined the method of nanografting and dip-pen lithography and obtained high spatial resolution irrespective of the substrate and atmospheric conditions. A key factor that plays a major role in nanopatterning is the tip-surface interaction, which should be kept minimal and local.⁶ The best method to obtain general patterning in self assembled monolayer’s is by nanoshaving or by nanografting; however, the fate of the displaced molecules depends on the structure of the self assembled monolayer’s and the fabrication environment, which is a key factor to decrease the piling of the particles at the edges of patterns. If the local displacement and readsorption of the displaced particles is minimized sharp and clear patterns can be achieved. Wang and co-workers developed a dip pen lithographic technique in which they have specially designed a method that feeds the AFM tip with nanoparticles that acts as ink and are used to write the patterns over the substrate.⁹ By using this method they were successful in creating dots of 200 nm and lines of 100 nm. They used parafilm on top and under the probe to load the nanoparticles (i.e. the ink) that were dispersed in low viscous solvents such as water and methanol that were then evaporated by exposing the tip to 60-70⁰C under saturated water vapor environment.
Denis and co-workers described a method for preparing surfaces with well-defined nanoscale patterns. In their experiment they showed that nanopatterned surfaces display strong chemical contrast in the form of hydrophobic CH₃ nanopatches surrounded by a TiO₂ surface, or vice versa.³ They used chemically modified tips that offer advantages over the other normal lithographic techniques. Resch et. al. explained how to manipulate the structures using an AFM and build two and three dimensional nanostructures.⁴ They explained about mechanical pushing and specific rotation of the particles about an axis to obtain patterns. They used bifunctional organic molecules in combination with the AFM manipulation techniques to obtain high spatial resolution patterns. The nanoparticles were linked either by (i) forming a multiparticle structure and subsequent treatment with dithiols or by (ii) pushing together individual particles, which were treated with dithiols prior to manipulation.³,⁴

There are several different sizes of gold colloid particles available that can be used, but 5 nm particles are the most easily dispersed, which aids in patterning. The 5 nm particles adsorb with irreversible kinetics. The 5 nm particles adsorb to form a disperse submonolayer of individual particles with atomic force microscope images showing no evidence of aggregation.⁷
EXPERIMENTAL

Chemicals:

The following chemicals were used in this study in the grades specified below. Supplier details are also provided.

Nochromix™ is a mixture of reagent grade concentrated sulfuric acid (Fisher Scientific, Fair Lawn, NJ) and a proprietary formulation of detergents and ammonium persulfate from Godax Laboratories (Cabin John, MD). It is a very strong oxidizer and should be handled with great care.

Potassium hydrogen phosphate and ACS grade methanol were purchased from Sigma Aldrich Inc. St. Louis, MO.

ACS grade nitric acid, citric acid, potassium phosphate, and sodium sulfate were purchased from Fischer Chemicals.

Type I deionized water was prepared using a Barnsted-Thermolyne Nanopure II system and had a specific resistivity of greater than 16.7 MΩ at delivery.

Poly-(diallyldimethylammonium chloride) (PDDA) was purchased from Aldrich Chemical (St. Louis, MO) in the following four varieties:

- Very Low molecular weight (< 100,000 g/mol) Batch # 10327DE
- Low molecular weight (100,000 – 200,000 g/mol) Batch # 08417JE
- Medium molecular weight (200,000 – 350,000 g/mol) Batch # 07316BH
- High molecular weight (400,000 – 500,000 g/mol) Batch # 13502ME
Ultra High Purity Argon gas (UHPAr) was supplied by Air Gas Inc.

Potassium bromide was purchased from Merck & Co., Inc. Rahway, NJ.

Potassium iodide was purchased from Mallinckrodt Chem., St.Louis, NY.

Sodium Fluoride was purchased from Matheson Coleman & Bell, Norwood, OH.

Silanization solution: 5% Dimethyldichlorosilane and 95% Heptane.

Equipment:

FisherBrand microscope slide cover slips (12-543-C 22X50 – 2) were purchased from Fisher Scientific Inc.

4 mL vials (cat # 033917B) were purchased from National Scientific Company Inc. with caps made from white urea F217/Teflon lined. These were used to contain the slides and those used with gold colloid solutions were siliconized to prevent the colloid particles from adhering to the glass surface.

The atomic force microscope used in this study was a Molecular Imaging (Tempe, AZ) PicoPlus with a 100-µm XYZ closed-loop scanner and a PicoScan 3000 controller.

MSCT AFM tips were purchased from Veeco Probes, Camarillo, CA.

Budget Sensors Multi-75 AFM tips were purchased from Nano and More USA, Lady’s Island, SC.
**Substrate Preparation:**

This procedure was taken from Hrapovic, et al\(^5\) and modified to improve its safety. A schematic of this process is shown in Flow Chart 1.

1. 25 × 50 mm cover slip scored and exposed to methanol vapor for 2 hours in Soxhlet apparatus

2. Snapped into seven individual slides

3. 50% HNO\(_3\) 30 minutes; rinsed with Type I water; dried with UHPAr
   Nochromix\(^\text{TM}\) 45 min; rinsed with Type I water; rinsed with methanol;
   Rinsed with 70°C Type I water; dried with UHPAr
   Negatively charged surface maximized

4. Exposed to PDDA solution for 2 hours
   Rinsed with Type I water; dried with UHPAr

5. Exposed to colloid solution for 24 hours

6. Rinsed with Type I water; dried with UHPAr
A 50 × 24 × 0.22 mm microscope slide cover slip (the substrate) is scored into seven equal sections, taking care that the cover slip does not break. The scored substrate is degreased by exposure to methanol vapors for two hours in a Soxhlet extractor.\(^5\)

The substrate is then snapped across the scored lines and the resulting pieces (slides) are placed in 50% nitric acid for 30 minutes. The slides are then washed with Type I deionized water and dried with a stream of ultra high purity argon gas (UHPAr). The slides are then placed in a Nochromix\(^\text{TM}\) solution for 45 minutes and then rinsed with Type I deionized water. This Nochromix\(^\text{TM}\) treatment was substituted in place of the use of the hot piranha solution (70:30 conc. H\(_2\)SO\(_4\):30% H\(_2\)O\(_2\)) specified by Hrapovic, et al.\(^5\) Nochromix\(^\text{TM}\) is a much safer alternative and has a longer shelf life than piranha. The slides are further rinsed with methanol followed by hot Type I deionized water and dried with a stream of UHPAr. This procedure removes any organic contamination from the slide and maximizes the exposure of negatively charged SiOH groups on the surface of the slide. This facilitates the adhesion of the polymer layer to the slide by allowing for greater interaction between the SiOH groups on the slide and the quaternary ammonium groups in the polymer.\(^5\)

The slide is then placed in a poly (diallyldimethylammonium chloride) (PDDA) solution for a period of 120 minutes. After the adsorption of the PDDA, the slide is then rinsed in Type I deionized water and dried using a stream of UHPAr. From this point some slides were treated with solutions of the potential blocking agents while others were transferred directly to the colloid adsorption step. Those slides that were treated with the potential blocking agents were exposed to a few drops of a 1.0 M solution of the compound and allowed to air dry. The gold colloid adsorption is accomplished by
placing the slide in a solution of the appropriate colloid for 24 hours. The slides are then rinsed with Type I deionized water, dried under a stream of UHPAr, and stored in a glass vial until they are scanned and/or modified using the atomic force microscope.

**Optimization of PDDA Molecular Weight, Adsorption Time, Gold Colloid Particle Size and Adsorption Time:**

The PDDA molecular weight, the time the slides were exposed to the PDDA solutions, the size of the gold colloid particles, and the time the slides were exposed to the colloid solutions were systematically investigated to find the optimal set of conditions for producing slides that were the most amenable to lithographic patterning. A full grid approach was utilized and each combination was investigated on the basis of the distribution of the colloid particles and whether or not they could be patterned with a Multi-75 AFM tip having a spring constant of ~3 N/m. The PDDA molecular weights investigated were very low molecular weight PDDA (VLPDDA, avg MW <100,000 g/mol), low molecular weight PDDA (LPDDA, avg MW 100,000 – 200,000 g/mol), medium molecular weight PDDA (MPDDA, avg MW 200,000 – 300,000 g/mol), High molecular weight PDDA (HPDDA, avg MW >300,000 g/mol). PDDA exposure times were from 60 to 240 minutes. Gold colloid particles of 2 nm, 5 nm, 10 nm, and 20 nm were investigated along with exposure times ranging from 6 to 48 hours.

**Modifications of the Slide Preparation Procedure:**

When using slides that are normally prepared, the force constant of the AFM tip required to pattern the slide is approximately 3 N/m. This results in severe blunting of the
tip, piling of the colloid particles on the edges of the patterned area, and potential damage to the PDDA layer. Several approaches were tried in order to circumvent these problems.

In one trial, a diamond tipped glass scorer was used to draw lines on the PDDA layer with enough force such that patterning of the PDDA layer took place. Then the PDDA patterned slide was placed in the gold colloid solution for 24 hours to deposit the colloid particles.

In another trial, an attempt was made to block the adsorption of the gold colloid by placing an obstacle (glass) on the PDDA layer.

In a third trial, a thin copper wire was tied to the PDDA coated glass slide and then exposed to the colloid solution.

The most effective method was the introduction of other ions to the PDDA layer prior to the colloid particle adsorption. These ions are referred to as potential blocking agents and are intended to reduce the binding forces between the PDDA layer and the colloid particles. Several compounds were used in this investigation, including potassium bromide, potassium iodide, potassium hydrogen phosphate, potassium phosphate, sodium fluoride, sodium sulfate, and citric acid.

The images of the prepared slides were obtained by using the atomic force microscope. Sharp and clear images can be obtained by optimizing the tip velocity, the force set point value, and the primary and integral feedback gains on the z-peizo. When the sample is imaged with a minimal force set point, a sharp image can be obtained. In contrast, if the force set point is increased, that leads to the patterning of the sample. A
simple pattern can be achieved by raising the force set point value while keeping all other values as they normally would be during imaging.
RESULTS AND DISCUSSION

Optimization of PDDA Molecular Weight, Adsorption Time, Gold Colloid Particle Size and Adsorption Time

With the goal of finding optimal conditions for producing colloid coated surfaces amenable to lithographic modification, four parameters were systematically varied: the molecular weight of the PDDA, the adsorption time of the PDDA, the gold colloid particle size, and the adsorption time of the gold colloid particles. The results are summarized in Table 1 and described in detail below.

**PDDA Adsorption Time.** The PDDA adsorption time was studied over the range of 60 to 240 minutes. When the slides were exposed to PDDA for 60 or for 90 minutes, a non-uniform polymer layer was deposited over the substrate. This resulted in an equally non-uniform distribution of the colloid particles, making the slides not useful for patterning as seen in Figures 3.1 and 3.2.

With an adsorption time of 120 minutes and of 150 minutes, uniform distribution of the polymer over the substrate was observed. When this substrate was coated with colloid particles, a uniform distribution of the particles was also observed and the slide was suitable for patterning as seen in Figures 3.3 and 3.4.

With PDDA adsorption times of 180 minutes or longer, the polymer was observed to clump significantly, perhaps due to a nucleation effect. When this substrate is exposed
to colloid particles, a relatively uniform distribution of the particles was observed. However, due to the clumps of PDDA, the colloid particles appeared in clustered formations as seen in Figure 3.5. Therefore, these substrates were not suitable for patterning.

**Gold Colloid Adsorption Time.** The gold colloid adsorption time was studied over the range of 6 to 48 hours. For all adsorption times under 18 hours, very little adsorption was observed. Once the adsorption time reached 18 hours, some particles were observed to be present on the surface as seen in Figure 3.6. A uniform layer is observed when the slides are exposed to the colloid solution for 24 hours. For adsorption times of 30, 36, and 48 hours there was no change in the layer of colloid particles, indicating that the surface is saturated with colloid particles when exposed for 24 hours.

**Optimization of Gold Colloid Particle Size.** Four sizes of gold colloid particles were studied to identify the particle size that yields the best favorability for patterning. When 2-nm particles were used, the patterning was easy but significant piling of the particles was observed at the edges of the patterned areas. This is likely due to a significant aggregation of the particles once they are disturbed from the surface by the AFM tip.

With 5-nm particles the patterns obtained were neat and clear. Less piling of the particles was observed at the edges of the patterns. When 10-nm colloid particles were used, a uniform layer was obtained over the PDDA, but patterning resulted in moderate piling of the particles at the edges of the patterns and a deviation at the edges of the patterned area was observed. The uniform distribution of the particles is as shown in
Figure 3.7. When 20-nm colloid particles were used to coat the PDDA, a uniform layer of colloid particles was observed; however, the force required to pattern was a bit higher than the force required for other particle sizes. Further, significant piling of the particles at the edges of the patterned area was observed along with the deviation of the patterned area at the edges as seen in Figure 3.8.

**PDDA Molecular Weight Optimization.** All four sizes of commercially available PDDA molecular weights were investigated. When very low molecular weight PDDA was used to coat the slides, the colloid particles were uniformly distributed to form a single layer over the PDDA. The apparent binding force between the PDDA and the colloid particles was not very high, as indicated by the relatively low force set point required for the patterning process as seen in Figure 3.9 with 5-nm colloids used. With the low molecular weight PDDA, the polymer coat was also uniform and the colloid particles were uniformly distributed over the PDDA layer. The force set point required for patterning was again minimal, which indicates that the binding force between the PDDA layer and the colloid particles is low.

With **medium molecular weight PDDA**, the polymeric coat was generally uniform but some roughness on the surface was observed as seen in Figure 3.10. Also, the force set point required to pattern is higher, which indicates that the binding force between the polymer and the colloid particles is higher. This is a less desirable surface for creating intricate patterns than those created by using the low or very low molecular weight PDDA.
With **high molecular weight PDDA**, the polymer coating exhibited repeated crests and troughs. The force set point required to pattern these was similar to that required with the medium molecular weight PDDA, again indicating that the binding force between the colloid and the PDDA is higher. The lack of general smoothness observed with the high molecular weight PDDA makes these slides generally unsuitable for regular patterning.

These experiments were repeated with nearly all the possible combinations of PDDA adsorption time, PDDA molecular weight, and colloid particle size while consistently using the 24 hour colloid particle adsorption time. The best results were obtained with a PDDA adsorption time of 120 minutes using low molecular weight PDDA and 5-nm colloid particles. All further experiments described here utilize these optimum conditions.
Table 1. Results of the optimized parameters with different combinations

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>VLPDDA</th>
<th>LPDDA</th>
<th>MPDDA</th>
<th>HPDDA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 nm</td>
<td>10 nm</td>
<td>20 nm</td>
<td>5 nm</td>
</tr>
<tr>
<td>60</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>90</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>GOOD</td>
</tr>
<tr>
<td>120</td>
<td>GOOD</td>
<td>GOOD</td>
<td>NS</td>
<td>GOOD</td>
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<td>150</td>
<td>GOOD</td>
<td>GOOD</td>
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</tr>
<tr>
<td>240</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
</tbody>
</table>

NS = Not Satisfactory
**Physical blocking of the colloid particles**

The reason for the adsorption of the colloid particles is the attraction between the PDDA layer (which has a positive charge) and the citrate stabilized gold colloid particles (which have a negative charge). If the parameters are modified, there will be a change in the binding behavior.

When the PDDA layer was patterned with a diamond-tipped glass scorer and then exposed to the colloid particles, it did not give any desired results; instead the particles were coated onto the edges of the patterned line. This result is illustrated in Figure 3.11.

When an obstacle such as a glass slide was used to block the coating of the colloid particles onto the PDDA, the blocking slide was unstable and slid across the PDDA layer. The exact reason for the sliding of the blocking slide was not determined, but this method was unable to block the colloid particles from coating the PDDA layer as shown in Figure 3.12.

When the blocking experiment is done by tying a copper wire onto the slide with the PDDA layer already present and exposing it to the colloid particles, blocking of the particle adsorption was not observed. Instead, a uniform layer of the particles was obtained.

**Chemical Blocking of the Colloid Particles**

Several compounds, primarily salts, were used to treat the PDDA layer prior to the adsorption of the gold colloid particles. This was initially conceived as an attempt to completely block the adsorption of the gold colloid particles; however, none of the
treatments have thus far effected a complete blocking of the PDDA surface. The treatment procedure was covered in detail in the Experimental section.

Although no complete blocking was achieved, a significant softening of the interaction between the gold colloid particles and the PDDA surface was found. The amount of softening of this interaction is estimated by the spring constant of the softest AFM tip that will produce patterns. In the native system where chloride is the anion present at the surface, an AFM tip with a spring constant of ~3 N/m is required.

When potassium bromide is used as the potential blocking agent, the dispersion of the colloid particles is uniform and patterning was possible with a 0.03 N/m tip. However, some deviations in the desired pattern were observed; flakes of particles were removed from the patterned area as shown in Figures 3.16, 3.17, 3.18, 3.19 and 3.20.

With potassium iodide, the dispersion of the colloid particles was uniform, but colloid particles were removed in groups during patterning. The patterned area was also distressed along the edges and significant piling of the particles was observed at the edges as seen in Figures 3.22 and 3.23.

With potassium hydrogen phosphate, the dispersion of the colloid particles was good but slight clumping of the particles was observed. Upon patterning, piling of particles and slight deviation from the desired pattern area was observed as shown in Figures 3.24, 3.25 and 3.26.

Citric acid showed relatively interesting results. The dispersion of the colloid particles was uniform and good over the PDDA layer. However, piling of the particles
was observed along the edges of the pattern as shown in Figures 3.27, 3.28 and 3.29 and a tip with a higher force constant (value N/m) was necessary to pattern this surface.

When **sodium fluoride** was used as the potential blocking agent, the dispersion of the particles was uniform but clumps of the particles was observed over the surface as shown in Figures 3.30, 3.31 and 3.32. A moderate amount of piling of the particles was observed at the edges of the patterned area, but the spring constant of the tip required to pattern these slides is a bit higher than 0.03 N/m.

When **potassium phosphate** was used as the potential blocking agent, the dispersion of the particles was uniform and the force required to pattern was also less. The piling of the particles was confined to a thin line when compared with the above salts. The patterned images are clear and good as shown in Figures 3.33-3.37.

With **sodium sulfate** as the potential blocking agent, the dispersion of the particles was uniform as shown in Figure 3.38. Patterns can be made on this surface with almost no piling of the particles at the edges as shown in Figure 3.40. The patterned shape is also neat and clear. Because less force is required to pattern with this system, complex images should be attainable by using sodium sulfate to modify the PDDA surface.
Figure 3.1 AFM image of 60 minutes HMPDDA coat and 5 nm gold colloid
Figure 3.2 AFM image of 90 minutes MPDDA coat and 5 nm gold colloid

Figure 3.3 AFM image of 120 minutes LMWPDDA coat and 5 nm gold colloid
Figure 3.4 AFM image of 150 minutes LMWPDDA coat and 5 nm gold colloid

Figure 3.5 AFM image of 180 minutes LMWPDDA coat and 10 nm gold colloid
Figure 3.6 AFM image of 120 minutes LPDDA coat and 5 nm gold colloid for 18 hours

Figure 3.7 AFM image of 120 minutes MPDDA coat and 10 nm gold colloid for 24 hours
Figure 3.8 AFM image of 2 hour HPPDA coat and 20 nm gold colloid

Figure 3.9 AFM image of 2 Hours LPDDA coat and 5 nm gold colloid for 24 hours
Figure 3.10 AFM image of 120 minutes MPDDA coat and 10 nm gold colloid for 24 hours

Figure 3.11 AFM image of PDDA patterned using glass scorer
Figure 3.12 AFM image of slide over slide to block the coating of colloid particles

Figure 3.13 AFM image of simple LPDDA coated slide
Figure 3.14 AFM image of simple MPDDA coated slide

Figure 3.15 Digital camera image showing the lines formed by patterning PDDA layer by using glass scorer
Figure 3.16 AFM image showing the uniform dispersion of the particles using potassium bromide as a potential blocking agent
Figure 3.17 AFM image of the patterned area using potassium bromide as a potential blocking agent (Image I)

Figure 3.18 Profile line of the patterned area in Figure 3.17
Figure 3.19 AFM image of the patterned area using potassium bromide as a potential blocking agent (Image II)

Figure 3.20 Profile line of the patterned area in Figure 3.19
Figure 3.21 AFM image showing the uniform distribution of the particles using potassium iodide as a potential blocking agent
Figure 3.22 AFM image of the patterned area using potassium iodide

Figure 3.23 Profile line of patterned area in Figure 3.22
Figure 3.24 AFM image showing the uniform distribution of the particles using potassium hydrogen phosphate as a potential blocking agent
Figure 3.25 AFM image of the patterned area obtained using potassium hydrogen phosphate

Figure 3.26 Profile line of patterned area in Figure 3.25
Figure 3.27 AFM image showing the uniform distribution of the particles using citric acid as a potential blocking agent
Figure 3.28 AFM image of the patterned area obtained using Citric Acid as a potential blocking agent

Figure 3.29 Profile line of patterned area in Figure 3.28
Figure 3.30 AFM image showing the uniform distribution of the particles using sodium fluoride as a potential blocking agent
Figure 3.31 AFM image of the patterned area obtained using sodium fluoride as a potential blocking agent.

Figure 3.32 Profile line of patterned area in Figure 3.31
Figure 3.33 AFM image showing the uniform distribution of the particles using potassium phosphate as a potential blocking agent
Figure 3.34 AFM image of the patterned area obtained when Potassium Phosphate is used as potential blocking agent (Image I)

Figure 3.35 Profile line of patterned area in Figure 3.34
Figure 3.36 AFM image of the patterned area obtained using potassium phosphate as a potential blocking agent (Image II)

Figure 3.37 Profile line of patterned area in Figure 3.36
Figure 3.38 AFM image showing the uniform distribution of the particles using sodium sulfate as a potential blocking agent

Figure 3.39 Digital camera image taken during patterning that shows MSCT C(0.01 N/m), D(0.03 N/m) and E(0.1 N/m) levers moving colloids and leaving patterns
Figure 3.40 AFM image of the patterned area obtained using sodium sulfate as a potential blocking agent (Image 1)

Figure 3.41 Profile line of patterned area in Figure 3.40
Figure 3.42 AFM image of the patterned area obtained using sodium sulfate as a potential blocking agent (Image II)

Figure 3.43 Profile line of patterned area in Figure 3.42
Figure 3.44 AFM image of the patterned area obtained using sodium sulfate as a potential blocking agent (Image III)

Figure 3.45 Profile line of patterned area in Figure 3.44
Figure 3.46 AFM image of WKU pattern
CONCLUSIONS

In summary, the following conclusions were found as a result of this work:

The optimum conditions that lead to efficient patterning are:

(i) Use of low molecular weight PDDA with a coating time of 120 to 150 minutes.

(ii) Exposure to 5-nm gold colloid for 24 hours

The dispersion of the colloid particles on the PDDA does not change when using the potential blocking agents compared to direct adsorption on the unmodified PDDA layer.

The most interesting potential blocking agents are the phosphate, sulfate and citrate salts, as they show some potential for modifying the adsorption of the gold colloids on the PDDA in a very favorable way.

The use of the potential blocking agents reduces the force required to pattern by a factor of 100 to 300.
FUTURE WORK

In order to better quantify the forces required for patterning with different potential blocking agents, it would be beneficial to measure the force constant of each individual tip that is used to pattern the slide. With these measurements and the force set point reading from the AFM, the actual force or a number proportional to the actual force could be calculated.

In order to gain a better understanding of the areas that are patterned, it would beneficial to image the patterned area a new tip to remove the artifacts of the blunted tip from the images. The blunting of the tips could also be measured by using them to image a well-known or well characterized surface after using them for patterning. This would allow for better understanding of the wear on the tip that occurs during patterning.

Ultimately more intricate patterns such as interdigitated arrays should be pursued for use in sensors. Controlling the placement of the PDDA onto the glass surface via screening printing or ink jet methods to allow more direct and spatially control patterning to be achieved.
BIBLIOGRAPHY


