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Development of Colloid Displacement Lithography Platforms for Sensor Applications

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DEVELOPMENT OF COLLOID DISPLACEMENT LITHOGRAPHY PLATFORMS
FOR SENSOR APPLICATIONS

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

In Partial Fulfillment
Of the Requirements for the Degree
Master of Science

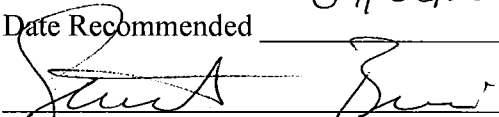
By
Mahesh Thugu

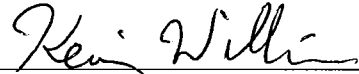
August 2013

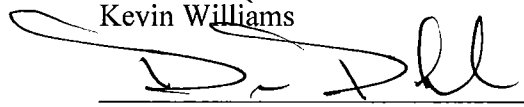
DEVELOPMENT OF COLLOID DISPLACEMENT LITHOGRAPHY PLATFORMS
FOR SENSOR APPLICATIONS


Date Recommended

07/03/2013


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Date

I dedicate this thesis to my parents Gopal Reddy and Swarna, Lethika and Padmakumar
my brother Raj, my adviser Dr. Stuart Buris, my friends Harsha, Srujan and Raja who
supported and encouraged me the most during my challenging times at Western
Kentucky University.

ACKNOWLEDGMENTS

This thesis would not have been possible without the guidance and help of several individuals who in one way or another contributed and extended their valuable assistance in the preparation and completion of this study. Firstly I thank the Almighty for giving me the courage and perseverance in completing the thesis. I would also like to express my utmost gratitude to my adviser Dr. Stuart Burris, for his continuous support and encouragement throughout my stay at Western Kentucky University. I would like to thank my committee members, Dr. Darwin Dhal and Dr. Kevin Williams for their willingness to help and having patience to conduct the final revision of my thesis. I am grateful to all the professors who helped me throughout my course work. I acknowledge the Department of Chemistry for recruiting me into their graduate program and providing the teaching assistantship. I appreciate Dr. John Andersland for helping me in using the optical microscope. Last but not least I would like to express my deep sense of gratitude to my dear parents for being my pillar of strength providing me their moral support and encouragement in helping me finish this research to achieve my goal. I would also like to thank all my friends, whose direct or indirect help has enabled me to complete this work successfully.

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DEVELOPMENT OF COLLOID DISPLACEMENT LITHOGRAPHY PLATFORMS FOR SENSOR APPLICATIONS

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In this work, Poly (diallyldimethylammonium) chloride - (PDDA) was used as a base layer for developing colloid displacement lithography platforms for sensor applications. Previous work shows that glass coated with PDDA and exposed to gold acts as a good platform for colloid displacement lithography. However, for actual sensor applications, electrical isolation of individual sensor sections must be achieved. This is attempted by laying down a 40 μm stripe of PDDA on a cleaned substrate and coating that stripe with gold colloid. The size of 40 μm or less in width is set as the target to fit within the scan window of the AFM. Stripes wider than about 40 μm would be difficult to efficiently pattern with colloid displacement lithography.

While the goal of 40 μm wide stripes was achieved with sufficiently diluted PDDA solution, it was found to be difficult to adsorb sufficient amounts of gold colloid on those stripes before the stripes were lost from the glass substrate. Further, electroless deposition was found to produce only a small amount of gold on the PDDA surface without colloid nucleation sites being present.

INTRODUCTION

The process of printing an image or text on the flat surface of limestone or metal plate is known as lithography.¹ Nanolithography is one of the sub-technologies of nanotechnology. Nanotechnology is used in many processes in day to day life and is found to be important in fabrication of memory devices, display units, biosensors and integrated circuits. Nanolithography is also used to study the fabrication of structures at the microscopic level.² Nanofabrication refers to fabrication of nanometer size features in materials and with molecules where functional units of less than 100 nm in size are constructed³.

Biosensors are the most commonly used devices for detection of biological analytes such as glucose, lactose etc. They are very useful for clinical applications and they are commercially important. In the last ten years, biosensors have been extensively used for micrometer and sub-micrometer level investigations. They are used as multianalyte sensing devices in intensive care units and operation theaters, as they can measure an analyte under physiological conditions. They are also used by diabetic patients for daily checks of glucose levels in blood⁴. They can also be used to study the glucose uptake by individual cells and for monitoring metabolic processes. As such, many researchers have been using these types of sensors to make quantitative measurements by applying these biosensors on living cells, blood and other biological samples both *in vitro* and *in vivo*.⁵

There are an array of techniques which are used in this technology such as optical lithography, X-ray lithography, electron beam direct-write lithography, extreme

ultraviolet lithography, molecular assembly methods, atomic force microscope nanolithography, and charged and neutral particle lithography.²

Atomic force microscopy (AFM) is one of the important techniques that is used to image structures of nanometer size. AFM nanolithography is fast growing, and it continues to attract increasing interest in nanotechnology. AFM nanolithography has the ability to pattern a wide range of materials including metals, semiconductors, polymers and biological molecules in different media.⁶

AFM can also be used to move particles to create two dimensional patterns. In their review, Gorman et al reported many other uses of AFM. They gave much information on the visualization of surfaces at the molecular level and on the modification of surfaces as well.³ They described many techniques and identified their advantages and disadvantages by comparing their nanolithography capabilities. Various methods were reviewed that can produce successful patterns.

AFM allows the visualization of the arrangement of nanostructures in three dimensions. High resolution can be obtained from the vertical, or Z, axis and it is limited only by the vibrational environment of the instrument. Horizontal, or X-Y axis, resolution is limited by the diameter of the tip that is used for scanning the nanostructures. In material sensing mode, AFM can differentiate between different materials, providing spatial distribution information of nanostructures. The size, shape and periodic arrangement of nanostructures can be characterized in this way.

Hrapovic et al fused gold nanoparticles onto the surface of glass without any application of an electrical potential by a process of electroless deposition.⁷ A target surface is taken and placed into a plating bath solution. This solution consists of

complexed metal ions and a reducing agent. This combination reduces metal ions to deposit them on to the target surface without any applied voltage.⁸⁻¹⁰ The deposited particles are characterized by AFM, uv-visible spectroscopy and cyclic voltammetry to determine and examine the morphology. Electroless deposition allows the fabrication of printed circuits and hard disk memory.¹¹⁻¹²

Polymers are soft materials and they are used as masks or resists in many device fabrication processes. So there has been strong interest in the patterning of polymers by AFM nanolithography.¹³ In this work poly (diallyldimethylammonium) chloride - (PDDA) was used as a polymer and aimed at developing colloid displacement lithography platforms for sensor applications. Previous work shows that glass coated with PDDA and exposed to gold acts as a good platform for colloid displacement lithography. However, for actual sensor applications, electrical isolation of individual sensor sections must be achieved. It is achieved by laying down a stripe of PDDA of 40 μm width on a cleaned substrate and coating that stripe with gold colloid.

EXPERIMENTAL PROCEDURE

CHEMICALS: Unless otherwise specified, all chemicals used were of ACS Reagent Grade or higher quality. The chemicals listed below were used in various parts of the research.

- Four different molecular weights of poly (diallyldimethylammonium) chloride – PDDA – were used in this work (Aldrich Chemical). These were very low molecular weight (VLMW, <100,000 g/mol), low molecular weight (LMW, 100,000-200,000 g/mol), medium molecular weight (MMW, 200,000-350,000 g/mol), and high molecular weight (HMW, 400,000-500,000 g/mol). The solutions were all 20% by volume except for VLMW, which was 35% by volume.
- NoChromix: A commercially available powder containing ammonium persulfate and detergents that is dissolved in concentrated sulphuric acid. NoChromix is preferred over piranha solution due its longer shelf life and the fact that it is safer to handle than piranha solution.
- Type 1 deionized water with a resistivity of greater than 16.7 M Ω -cm.
- Ultra High Purity Argon Gas (UHP Ar) - UHP Ar is used to efficiently remove excess water from the substrates when necessary.
- Salinization Solution - 5% dimethyldichlorosilane in heptane. This is used for passivating the interior surface of the 4 mL glass vials used to contain gold colloid solutions.
- Gold colloid solution (5 nm diameter) from BBI solutions with part number EMGC5.
- H₂AuCl₄ – 0.01% solution from Sigma-Aldrich with part number 7440-57-5.
- Hydroxylamine hydrochloride from Sigma-Aldrich with part number 5470-11-1.

EQUIPMENT:

- PicoPlus AFM: The atomic force microscope used in this study for imaging the substrates was a Molecular Imaging PicoPlus AFM. PicoView software was used for instrument control in imaging.
- AFM tips: All-In-One silicon AFM probes were purchased from Budget Sensors. They can be used in several measurement modes, but the standard contact mode tip was used for all imaging done in this work.
- Picospritzer: The Parker Picospritzer III generates repeatable pressure pulses. It produces ejections of nanoliter to microliter volumes and was used to pump PDDA solutions onto substrates.
- The optical microscope that was used to measure the width of PDDA stripes was a LEICA MZ 16 stereo microscope. It has oblique bottom illumination from a fiber optic and a bright field / dark field base. The pictures were captured using a JVC KY-F75 U camera, which is interfaced with Syncroscopy Auto Montage software. This software was calibrated with a micrometer scale and then used to measure stripes.
- The optical microscope that was used to observe the stripes during application on the substrates was a Wild M40 inverted microscope with a 10X bright field objective.
- Capillary puller: PC10 puller from Narishige, Japan. It pulls the glass capillary vertically using the gravitational force of standard built-in weights. This puller produces long thin glass capillaries for injection purposes.
- Gwyddion (www.gwyddion.net) was the software application used for AFM image processing and analysis.

- Fisher Brand glass microscopic slides were used as the substrates in the initial experiments.
- Fisher Brand glass microscopic slide cover slips ($50 \times 24 \times 0.22$ mm) were used as the substrates in experiments utilizing gold colloid solutions.
- Glass 4-mL vials were used to contain all solutions used for processing the small sections of the microscope slide cover slips.
- UV-Visible spectrophotometer: A LAMBDA 850 UV/Vis Spectrophotometer from PerkinElmer was used to collect spectra for several of the cover slip substrates.

SUBSTRATE PREPARATION:

Two types of substrate were used. First was a microscope slide (25×75 mm) that was scored and later broken into two equal halves. The second type of substrate was a microscope slide cover slip (25×50 mm). The cover slip was scored to prepare seven equal pieces after the initial cleaning step described below.

For either case, the scored substrate was placed in a Soxhlet extractor and exposed to ethanol vapor for 2 hours. This scored substrate was removed from the extractor and broken into pieces along the score lines. Full microscope slides were broken into two equal halves (25×25 mm) and cover slips were broken into seven pieces ($\sim 7 \times 25$ mm). The smaller substrates were treated with 50% nitric acid solution for 30 minutes and then removed from the solution and washed with Type I deionized water. Then the substrates were exposed to freshly prepared NoChromix solution for 45 minutes. After the NoChromix treatment, the substrates were washed with Type I deionized water and further rinsed with methanol and then hot Type I deionized water. These substrates were

dried under a stream of ultra-high purity argon gas (UHP Ar). This process cleans the substrate and promotes the exposure of negatively charged silanol groups on the surface of the slide. This facilitates polymer layer adhesion on the surface of the slide via electrostatic interaction between the silanol and the quaternary ammonium groups in the polymer.

PDDA STRIPE APPLICATION:

A substrate that is cleaned up to the hot methanol step was placed on the microscopic stage of the Wild M40 microscope. A capillary tube of 1 mm in diameter was inserted into the coil of the capillary puller, where it was exposed to heat inside the coil for a period of 14 seconds. The resulting capillary tube was long and thin in its middle section. The two halves of the pulled capillary were separated using closed forceps. All grades of PDDA solution were injected into one of the pulled capillary tubes with the help of a 1 mL syringe. The Picospritzer was connected to UHP Ar and used to pump the PDDA solution. The stage of M40 microscope was set up so that the tip of the capillary tube was placed on the substrate present on the microscopic stage. This was then viewed through the microscope objective. The pressure on the PicoSpritzer was adjusted to 10 psi for a time period of 2 seconds. This pumped the PDDA from the capillary tube onto the microscopic slide. The microscopic stage was moved very quickly with the turning knobs, and the capillary tube drew the stripes on the substrate.

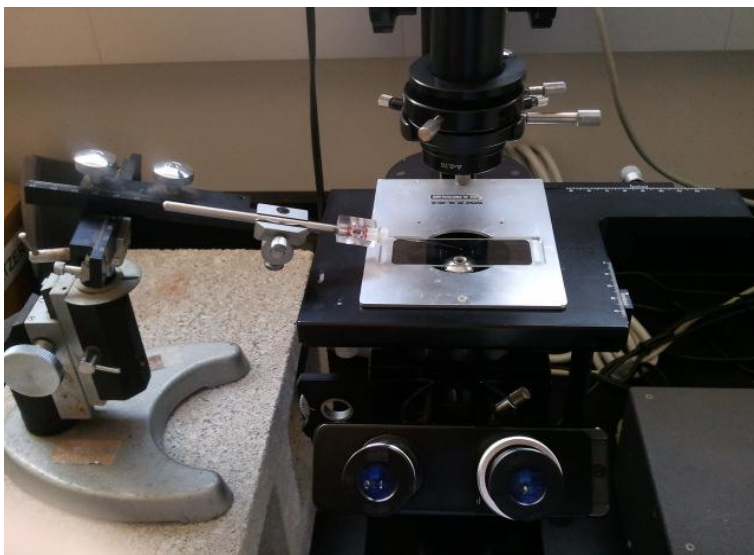


Figure 1 Set up showing PDDA stripe application.

VIAL CLEANING AND SILICONIZING:

Empty 4-mL vials were soaked in NoChromix solution for 30 minutes. The vials were removed from the NoChromix solution and thoroughly rinsed with Type I water. The interior of the vials were siliconized by a brief exposure of approximately 3 minutes to a 5% solution of dichlorodimethylsilane (DCDMS) in heptane. This process passivated the glass and prevented the gold colloid from precipitating out of solution. The siliconized vials were used in all gold colloid solution exposure steps with the cover slip substrates.

APPLICATION OF GOLD COLLOID:

For experiments with gold colloid, the vials described above are used. Exposure times to the 5 nm gold colloid varied depending on the particular experiment. Exposure times ranging from one minute to 24 hours were used in this work.

UV-VISIBLE SPECTROSCOPY:

UV-vis spectra were collected on selected cover slip substrates to determine the amount of gold colloid adsorbed onto the surface. A series of cover slips was investigated with UV-vis spectroscopy to determine how much gold was adsorbed. Five different substrate preparation levels were used.

1. A substrate cleaned through hot methanol (no PDDA or gold exposure)
2. A substrate exposed to PDDA for 2 hours to coat the entire substrate (no gold exposure)
3. A substrate coated with PDDA and exposed to gold colloid for 24 hours
4. A substrate cleaned through hot methanol and exposed to gold colloid for 24 hours
5. A substrate with PDDA stripes with 24 hour drying time and then exposed to gold colloid for 24 hours

All these cover slips were placed in a quartz UV-Vis cuvette with the help of closed forceps. UV-Vis spectra were collected between 350-800 nm.

ELECTROLESS DEPOSITION OF GOLD:

A 20 mL beaker was cleaned with NoChromix solution followed by thorough rinsing with Type I water. A solution of 0.05% HAuCl_4 and 0.4 mM hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) was poured in to the cleaned beaker and allowed to react. The reaction produced Au (0) on the surface at nucleation sites such as adsorbed gold colloid particles. Cover slip substrates were suspended in the electroless deposition

solution using self-closing forceps. Some deposition experiments utilized a spin vane and others had an unstirred solution. Once the deposition period concluded, the coverslip substrates were removed and dried with UHP-Ar.

AFM IMAGING:

AFM images were collected with a PicoPlus AFM using PicoView software in contact mode. The contact mode lever from an All-In-One silicon AFM probes was used for several substrates before wear became evident and it were discarded and replaced. Images were collected in three channels: topography, deflection, and friction. Only the topography images were selected for measurements and further processing.

AFM IMAGE PROCESSING AND MEASUREMENT:

AFM image processing was done using Gwyddion software. For all images, plane level subtraction was done, the minimum value was shifted to zero, and corrections for horizontal scars were made. For some images, a profile line was extracted from the image to better illustrate certain features. The widths of the PDDA stripes were measured from these profiles. Radius of curvature measurements were made via circle fits in Gwyddion.

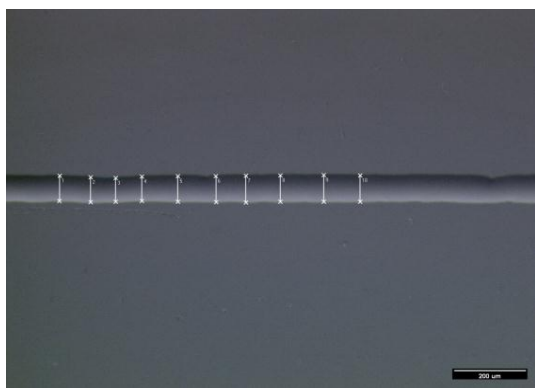
OPTICAL IMAGE COLLECTION AND PROCESSING:

Optical images were collected from the LEICA MZ 16 stereo microscope. The substrates were placed on a stage with a dark field base. The picture of the substrate was captured using a JVC KY-F75 U camera zoomed on to the stripe as close as possible. Syncroscopy Auto Montage software was calibrated with a micrometer scale and then

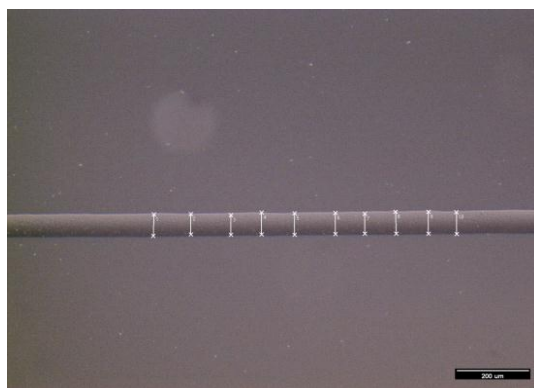
used to measure the stripes. Average widths were taken from multiple readings that were obtained on each stripe photographed.

RESULTS AND DISCUSSION

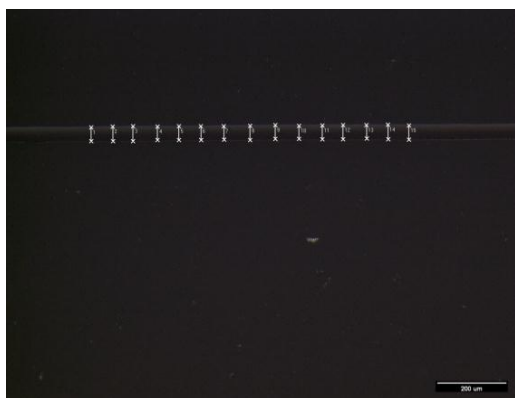
This work focuses on the development of colloid displacement lithography platforms for sensor applications. Previous work in this group has shown that glass coated with PDDA and exposed to gold colloid is a suitable platform for colloid displacement lithography. However, for actual sensor applications to work, electrical isolation of individual sensor sections or elements must be achieved. This could be done in one of two ways. The first approach is by laying down a stripe of PDDA on a cleaned substrate and then coating that stripe with gold colloid. The second approach is to coat the entire substrate with PDDA and then apply stripes of gold colloid solution on the fully coated surface. This work was aimed at the first approach where 40 μm wide PDDA stripes were produced on clean glass substrates. The size of 40 μm or less in width is set as the target to fit within the scan window of the AFM. Stripes wider than about 40 μm would be difficult to efficiently pattern with colloid displacement lithography. Stripes of PDDA of different molecular weights were drawn on microscope slide substrates as described in the Experimental Section. Initially, optical images were taken for these substrates with PDDA stripes to determine which molecular weight of PDDA produced the most desirable width for the stripes.



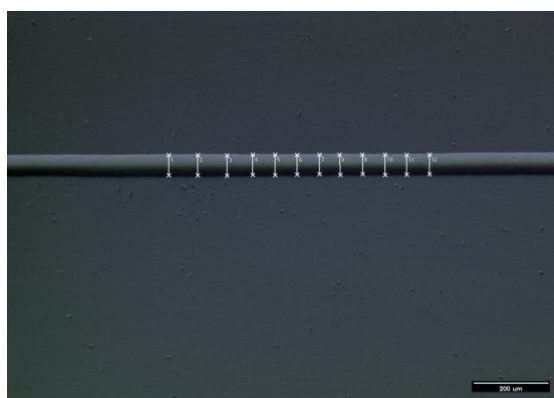
A



B



C



D

Figure 2.1 Optical images of PDDA stripes.

A-VLMW

B-LMW

C-MMW

D-HMW

PDDA TYPE	AVERAGE WIDTH OF STRIPES (μm)	NUMBER OF STRIPES AVERAGED
VLMV	76.29 ± 1.5	12
LMW	60.94 ± 1.8	15
MMW	37.45 ± 0.3	42
HMW	52.17 ± 1.2	36

Table 1 Table showing widths of stripes from all grades of PDDA.

Based on the measurement of the images, the stripes of medium and high molecular weight PDDA appeared to be more promising, as they were closer to the 40 μm width that is desired for later work.

Also, from previous work, it was determined that medium and high molecular weight PDDA perform better in the binding of gold nanoparticles. Therefore, medium and high molecular weights of PDDA were selected for further experiments to obtain stripes of 40 μm or less in width.

DILUTION OF PDDA:

High and medium molecular weight PDDA were chosen for further investigation, as they gave the best stripes ($< 40 \mu\text{m}$ wide). Pumping the stock MMW or HMW PDDA through the capillary tube was very difficult, as its high viscosity caused it to clog the capillary tube in a very short time. No PDDA comes out of the capillary tube after

drawing a few stripes, and the tip of the capillary has to be snapped with forceps in order to open the tip. As the tip is snapped, the width of the stripe increases because the width of the capillary increases.

In order to alleviate this problem, the PDDA solution was diluted with Type I water. The first series of dilutions was one part PDDA and two parts water (1:2 dilution), which produced 6.7% PDDA solutions. An additional series of dilutions was made at the 1:3 ratio, that produced a 5% PDDA solution. Stripes were drawn with both of these sets of dilutions, but it was found by visual inspection that the stripes spread significantly beyond the desired width of 40 μm .

The next series of dilutions were 2:1 and 3:1, which produced 13.3% PDDA and 15% PDDA, respectively. Measurements on optical images of these stripes were encouraging enough to warrant AFM imaging and measurements. In both cases (2:1 and 3:1) it was found that the viscosity of the mixture was favorable and that the stripes were accurately formed on the substrates. MMW performed better than HMW in both the dilution cases. As seen in Figure 2.2, the average width of 2:1 HMW PDDA was found to be 55.15 μm and the average width of 3:1 HMW PDDA was found to be 62.45 μm . Only MMW was chosen for further experiments. Optical images of 2:1 MMW PDDA in Figure 2.3 show the average width of the stripe is 50.43 μm . From the data shown in Figures 2.6 to 2.10, it is clear that the 3:1 dilution of MMW PDDA performed better than the 2:1 dilution. The 3:1 dilution of MMW PDDA consistently produced stripes in the 30 to 40 μm range.

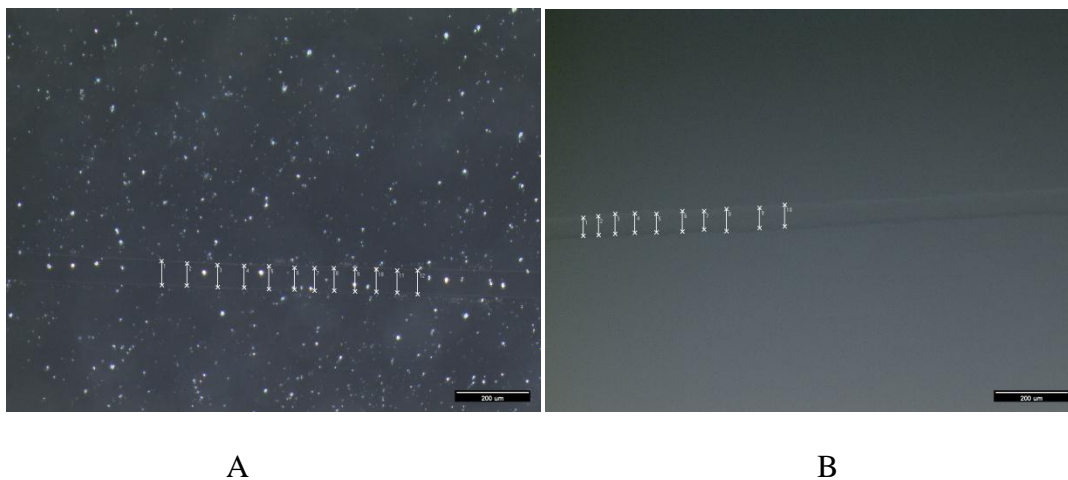


Figure 2.2 Optical images of HMW PDDA

A- 3:1 HMW PDDA B- 2:1 HMW PDDA

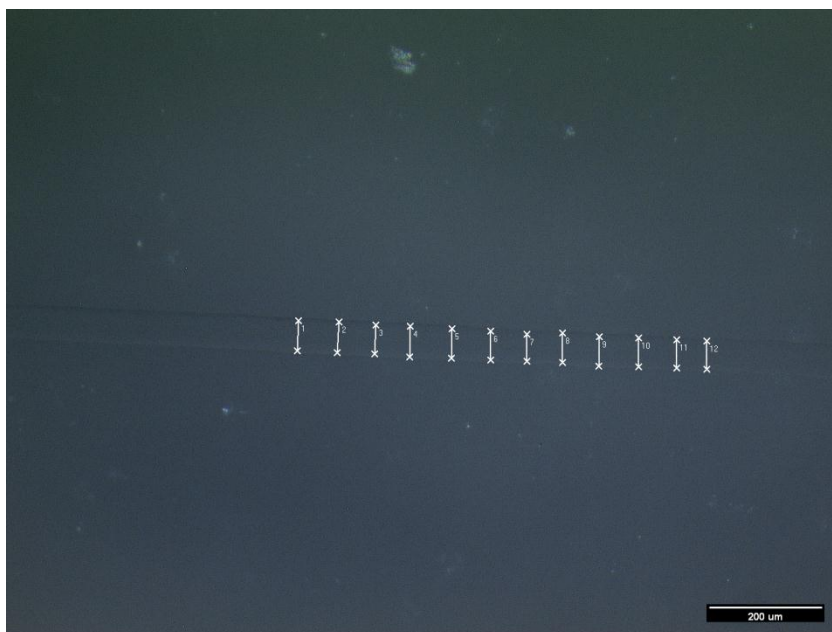


Figure 2.3 Optical image of 2:1 MMW PDDA

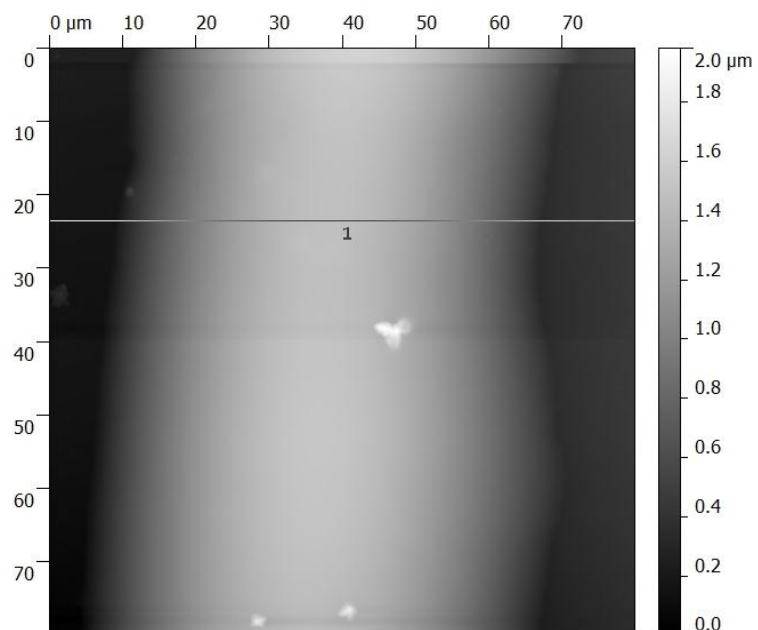


Figure 2.4 AFM image of 2:1 MMW PDDA stripe

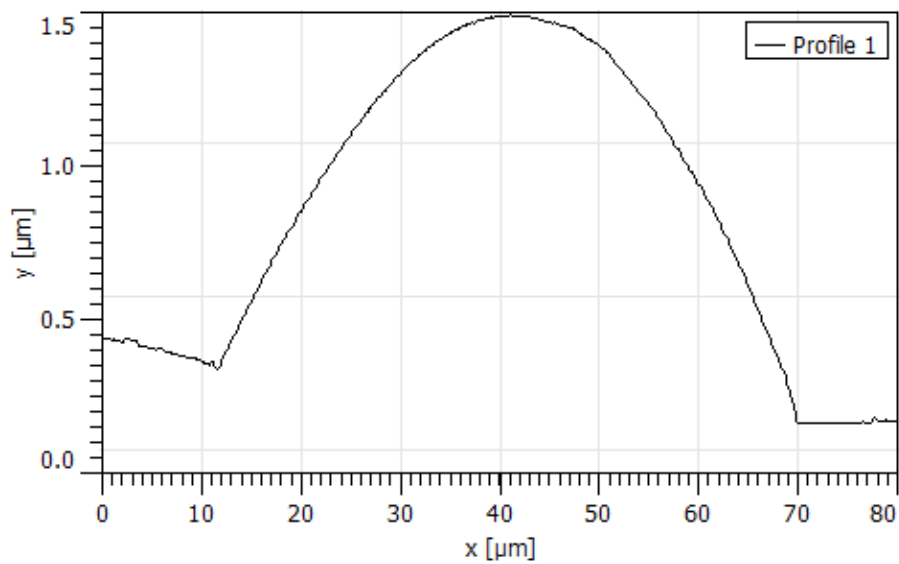


Figure 2.5 Profile line showing the width of the stripe in Figure 2.4

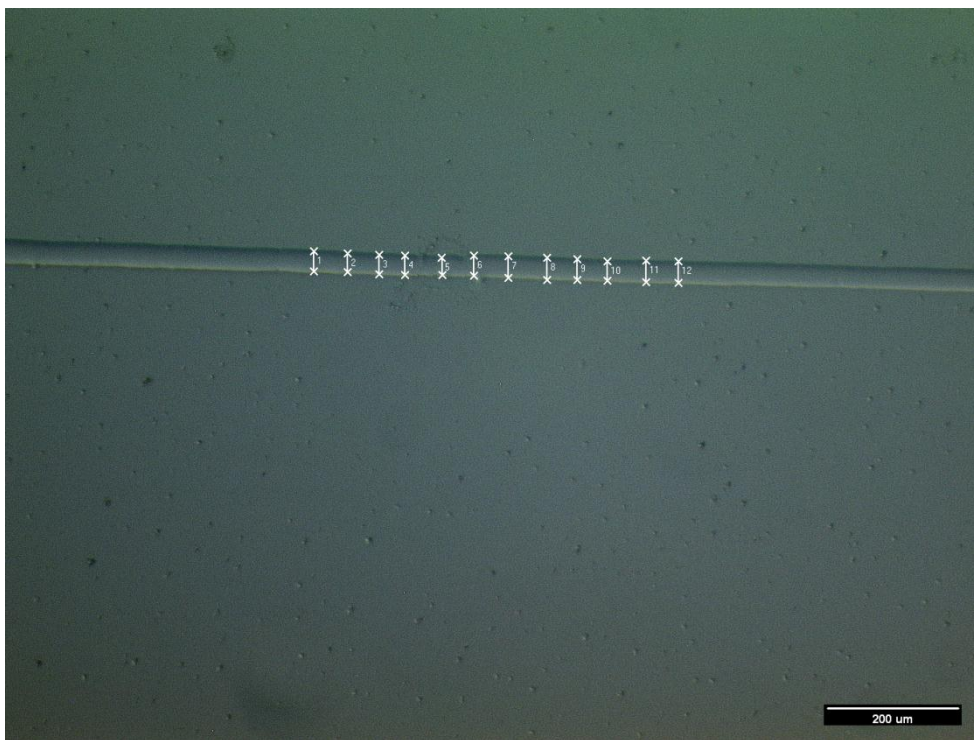


Figure 2.6 Optical image of 3:1 MMW PDDA stripe

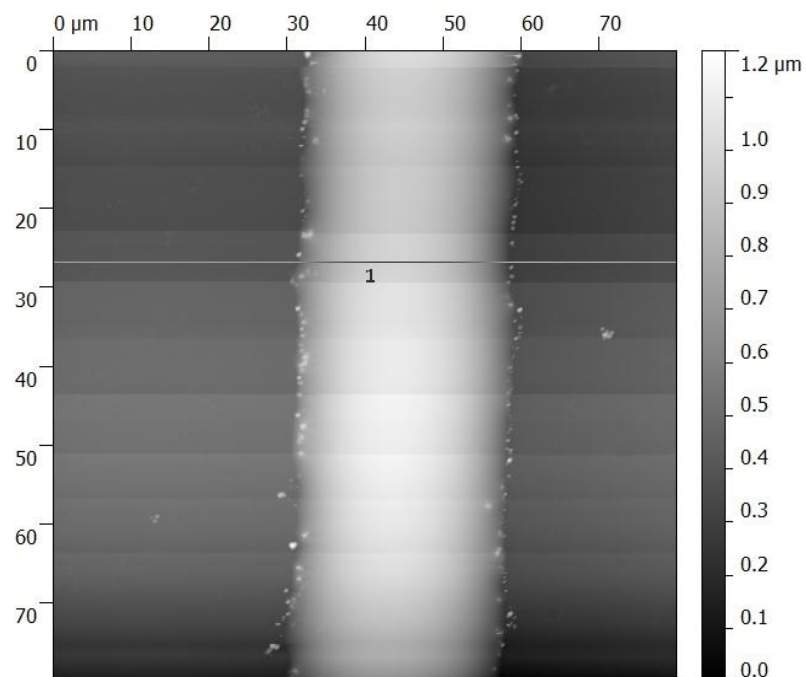


Figure 2.7 AFM image of 3:1 MMW PDDA stripe

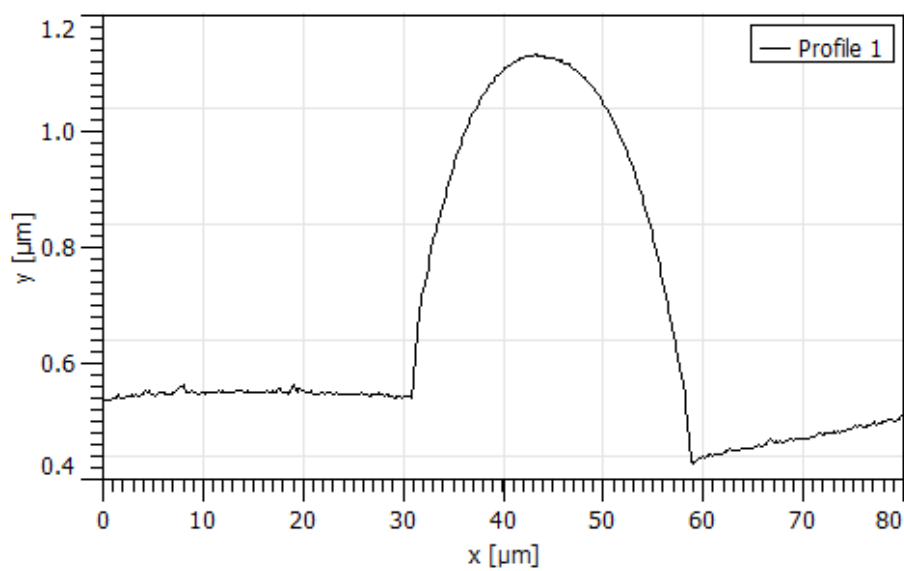


Figure 2.8 Profile line showing the width of the stripe in Figure 2.7

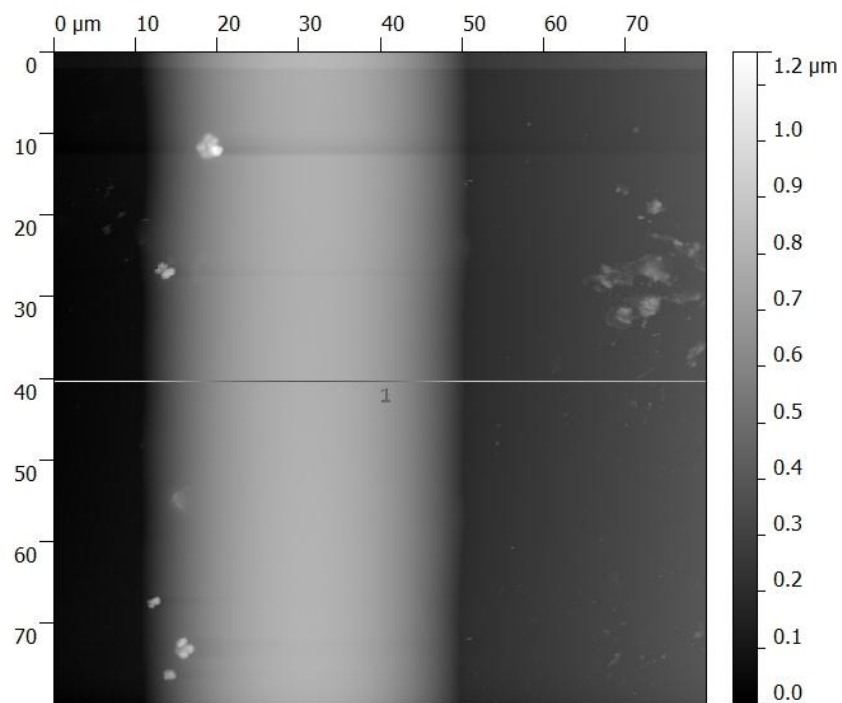


Figure 2.9 AFM image of 3:1 MMW PDDA stripe

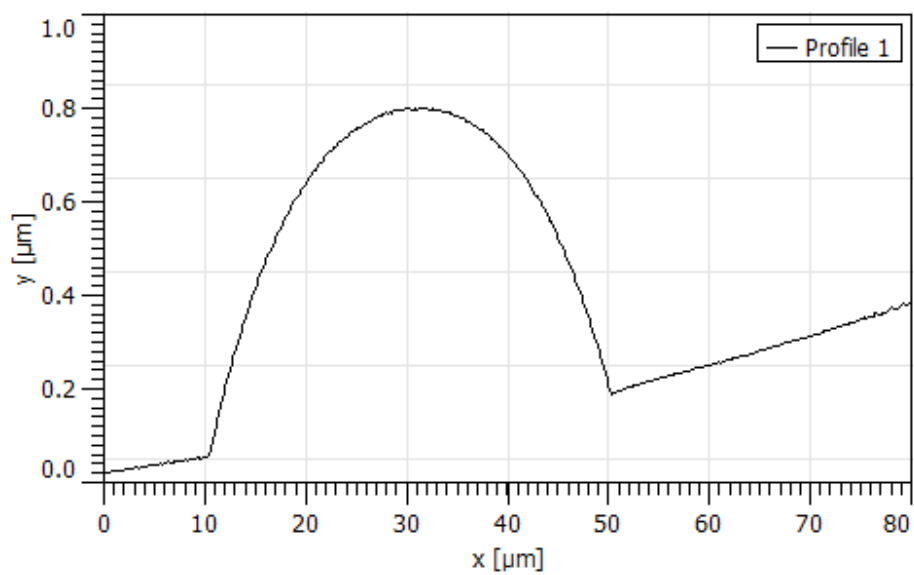


Figure 2.10 Profile line showing the width of the stripe in Figure 2.9

APPLICATION OF GOLD COLLOID:

Microscope slide cover slip sections ($\sim 7 \times 25$ mm), as described in the experimental section, were used in all subsequent experiments to limit the amount of gold colloid solution used.

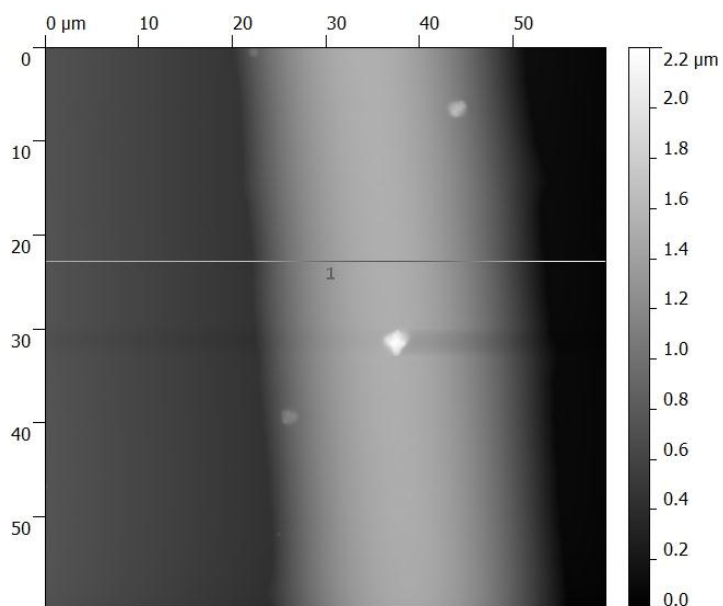


Figure 2.11 AFM image of 3:1 MMW PDDA stripe on second substrate

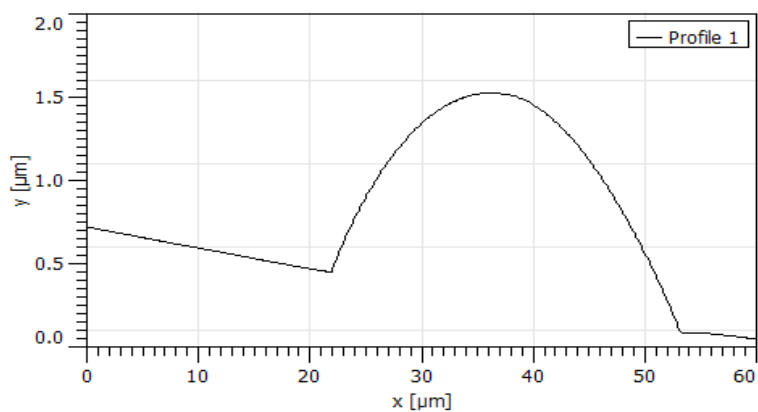


Figure 2.12 Profile line showing the width of stripe in Figure 2.11

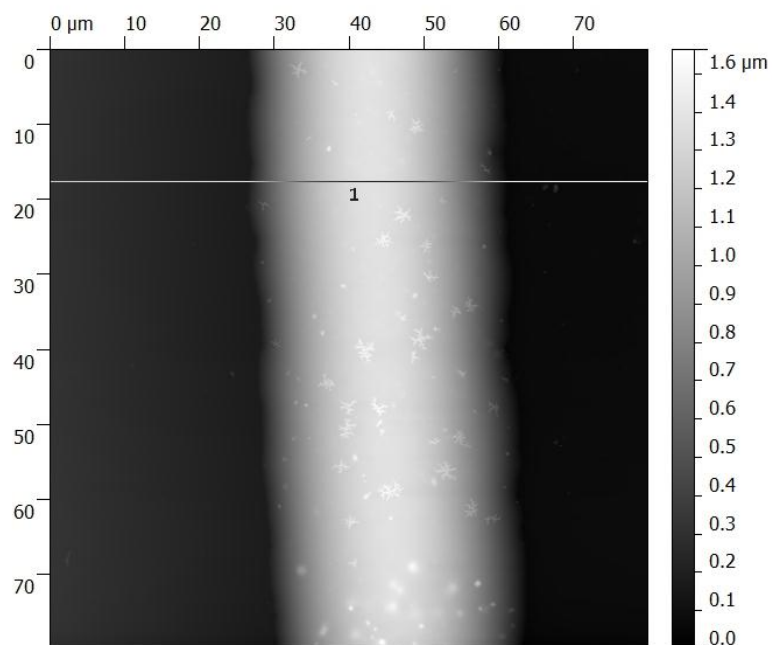


Figure 2.13 AFM image of 3:1 MMW PDDA stripe on second substrate.

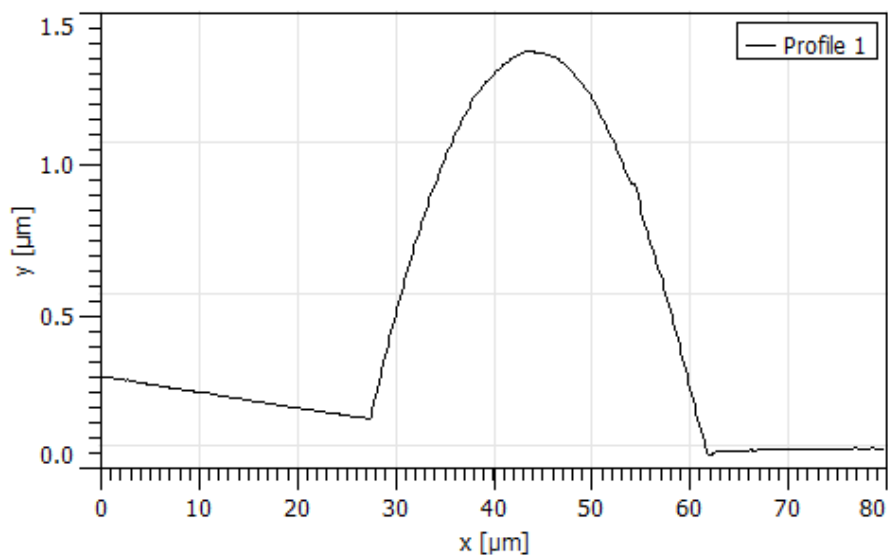


Figure 2.14 Profile line showing the width of stripe in Figure 2.13

The quality of the stripes on the cover slip substrates was verified by AFM imaging. From Figures 2.11 and 2.12, the width of the stripe is approximately 31 μm .

Also from Figures 2.13 and 2.14, the width of the stripe is approximately 34 μm . The height and radius of curvature were also measured along with the width of the stripe. The height and radius of curvature for Figure 2.11 are 1.24 μm and 100.14 μm , respectively. For Figure 2.13 they are 1.25 μm and 118.31 μm , respectively.

Cover slip substrates with 3:1 MMW PDDA stripes were placed in cleaned and siliconized 4-mL vials containing 5 nm gold colloid solution for 24 hours. After the 24 hours of incubation, it was observed that the stripes appeared to have dissolved into the gold colloid solution.

In order to determine the time required for dissolving the PDDA stripes into gold colloid solution, a series of cover slip substrates with PDDA stripes were placed into the gold colloid solution for short periods of time. The cover slip substrates were observed at one, three, five, and seven minutes. It was determined from this series of experiments that the stripes disappeared by the 5th minute. From the literature it was found that the thickness of a PDDA layer on a fully coated substrate is approximately 1.6 nm when rinsed with water or kept in a solution.¹⁴ This opens the possibility that the PDDA stripe is still present on the surface of the cover slip but is no longer visible to the eye or under optical microscope magnification levels.

ADSORPTION OF GOLD COLLOID ON PDDA STRIPES:

Additional cover slip substrates were striped with 3:1 MMW PDDA and dried for 24 hours. After the drying period, they were placed in vials containing 5 nm gold colloid

solution for 24 hours. AFM images were collected for the substrates exposed to gold for 1 minute and for 24 hours. There was no evidence of gold binding to the substrate with stripes and exposed to gold colloid solution for 1 minute (Figures 2.15 to 2.18). However, for the substrate with stripes exposed to gold for 24 hours, there was evidence of gold adhering to the polymer (Figure 2.19), as interpreted from the profile line of the image show in Figure 2.20.

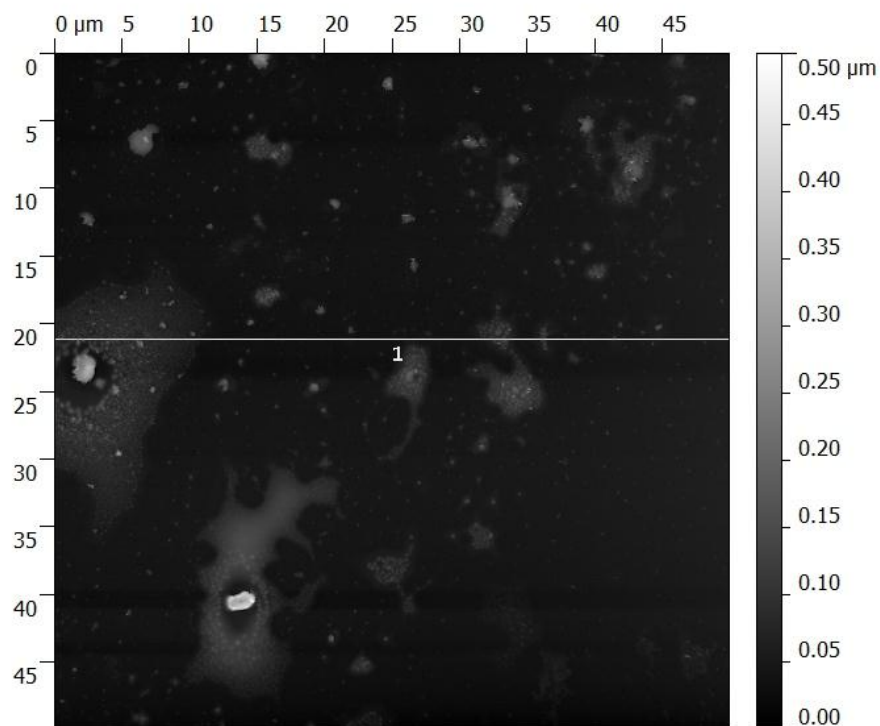


Figure 2.15 AFM image of 3:1 MMW PDDA stripe exposed to gold for 1 minute.

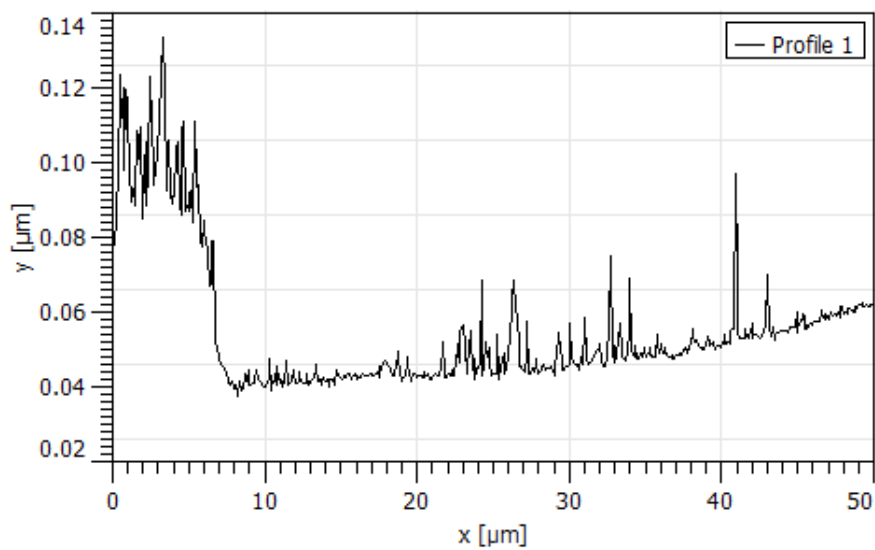


Figure 2.16 Profile line for the stripe in the Figure 2.15

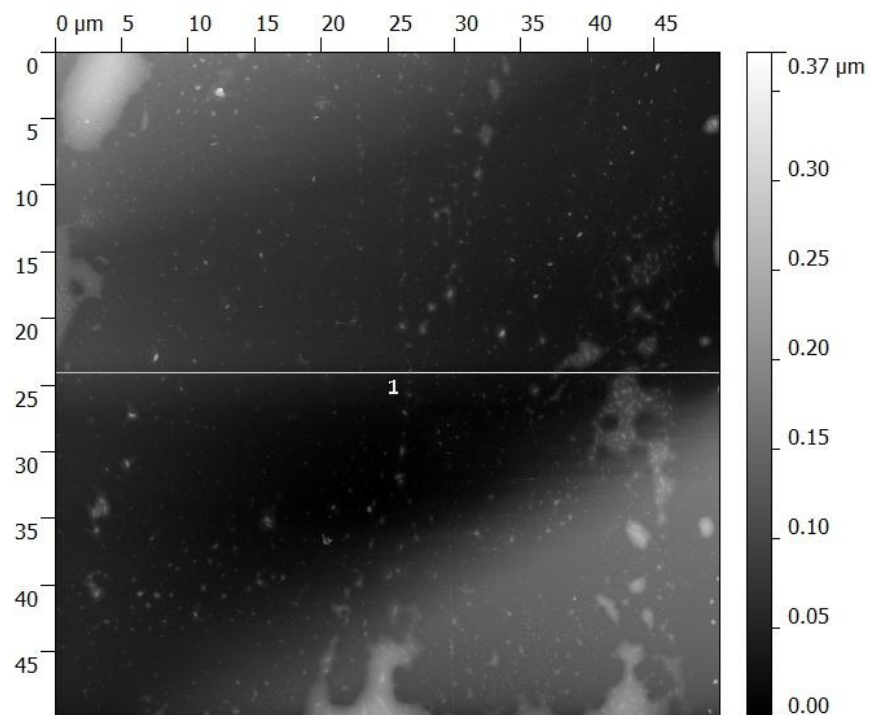


Figure 2.17 AFM image of 3:1 MMW PDDA stripe exposed to gold for 1 minute

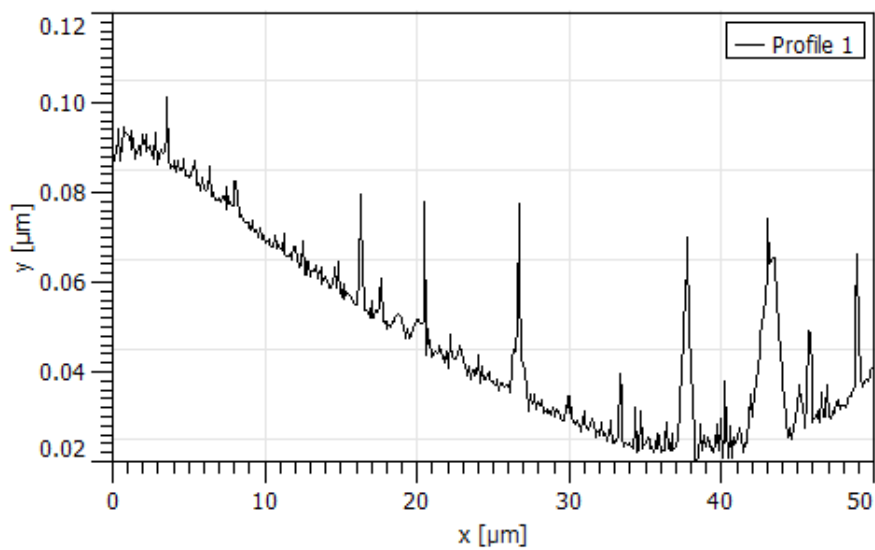


Figure 2.18 Profile line for the stripe in Figure 2.17

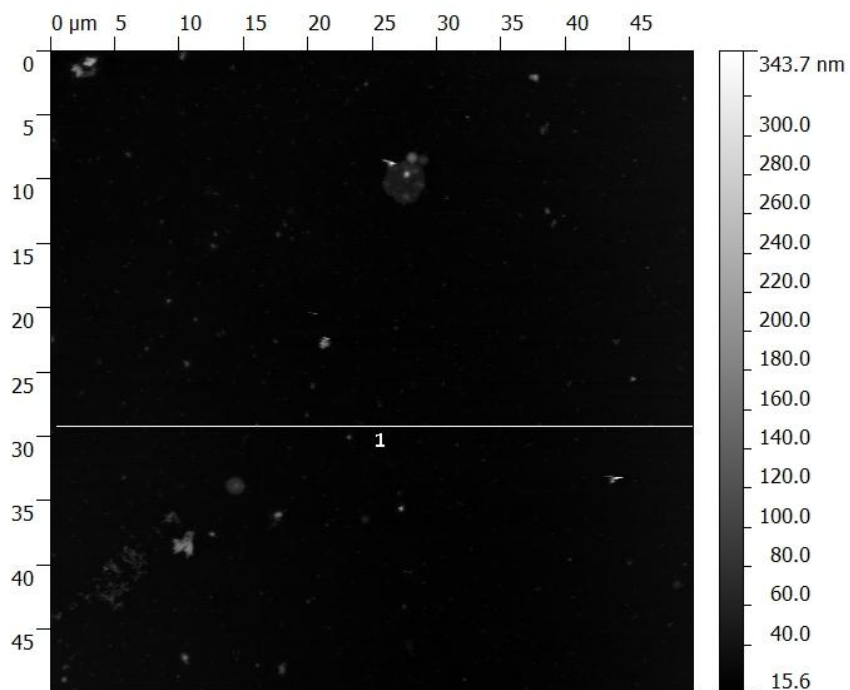


Figure 2.19 AFM image of 3:1 MMW PDDA stripe on substrate and exposed to gold for 24 hours.

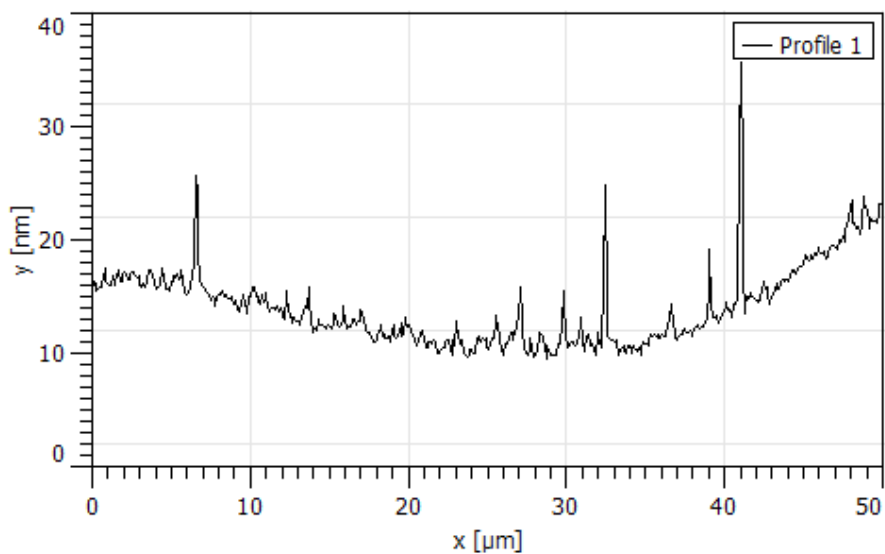


Figure 2.20 Profile line for the stripe in Figure 2.19

UV-Vis Investigation:

UV-Visible spectroscopy data and AFM data were collected on a series of cover slips at progressing levels of preparation as described in the experimental section. They were interpreted for evidence of the adsorption of gold colloid. Figures 2.21 to 2.30 show the AFM data collected for these samples. The spectra shown in Figure 2.31 show a significant rise in absorbance at ~550 nm (characteristic of 5 nm gold colloid) as the preparation level progresses from plain glass to PDDA coat to exposure to gold colloid. Evidence of gold is noted on the glass without PDDA, but it is small compared to the amount indicated by the spectrum from PDDA exposed to gold colloid (both full coat and stripes). The data in Figure 2.31 were manually adjusted to make the value of the spectra the same at 800 nm. This was done as a result of instrumental drift.

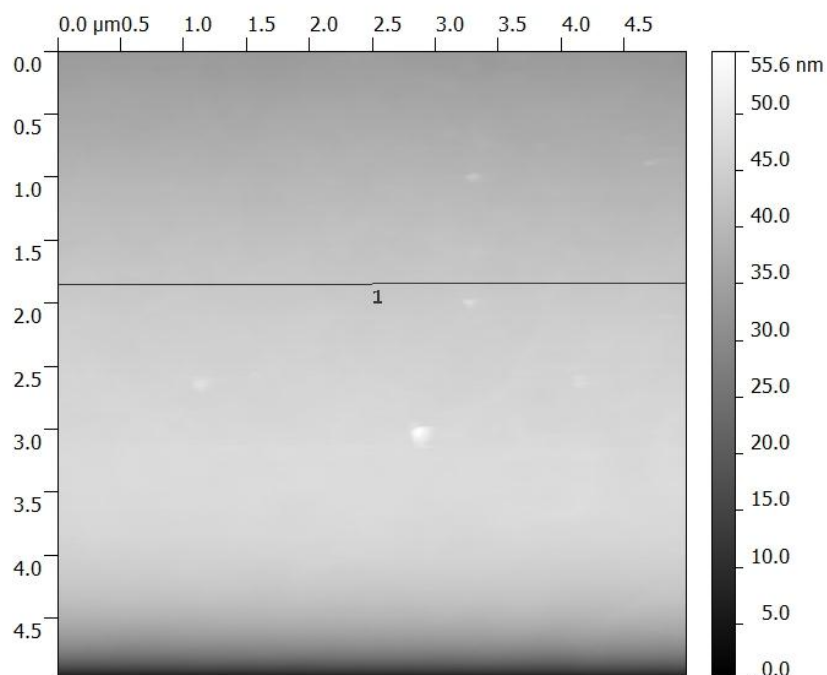


Figure 2.21 AFM image of cleaned substrate up to the hot methanol step

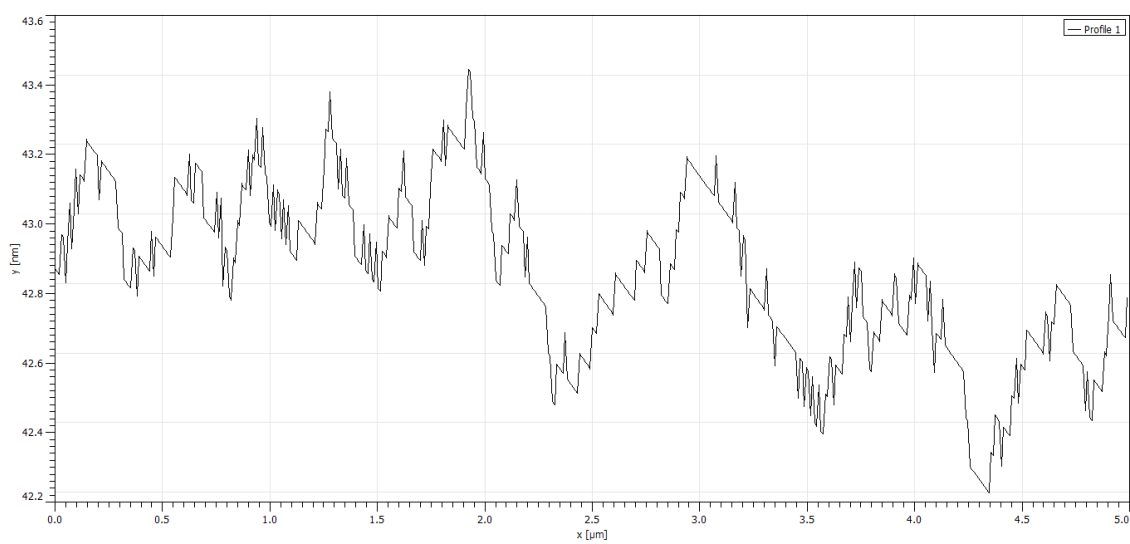


Figure 2.22 Profile line for the substrate in Figure 2.21

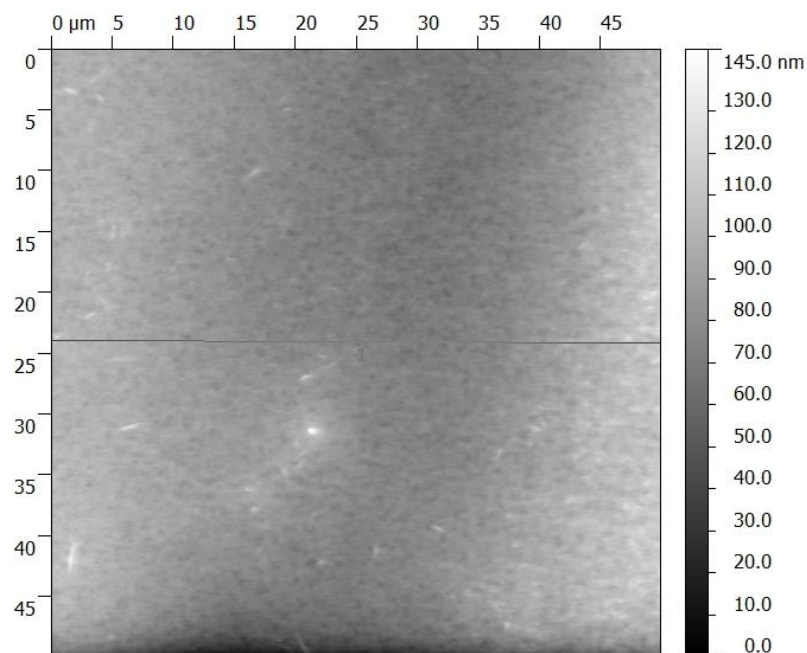


Figure 2.23 AFM image of substrate coated with PDDA

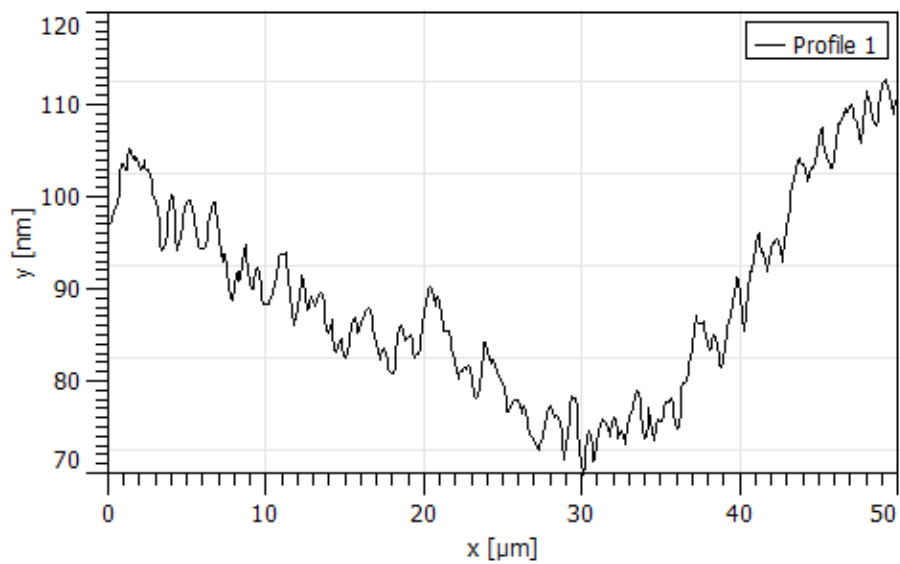


Figure 2.24 Profile line for the substrate in Figure 2.23

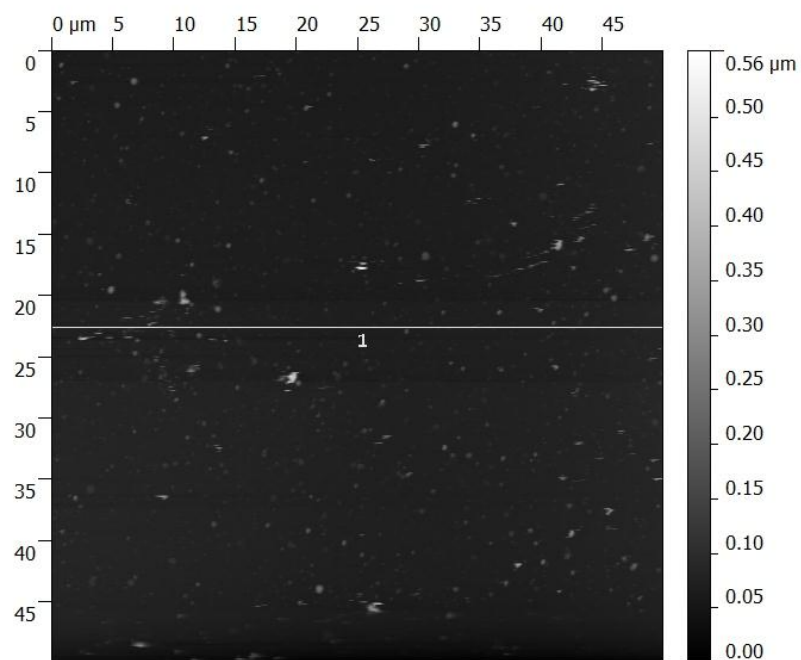


Figure 2.25 AFM image of substrate exposed to PDDA and gold for 24 hours

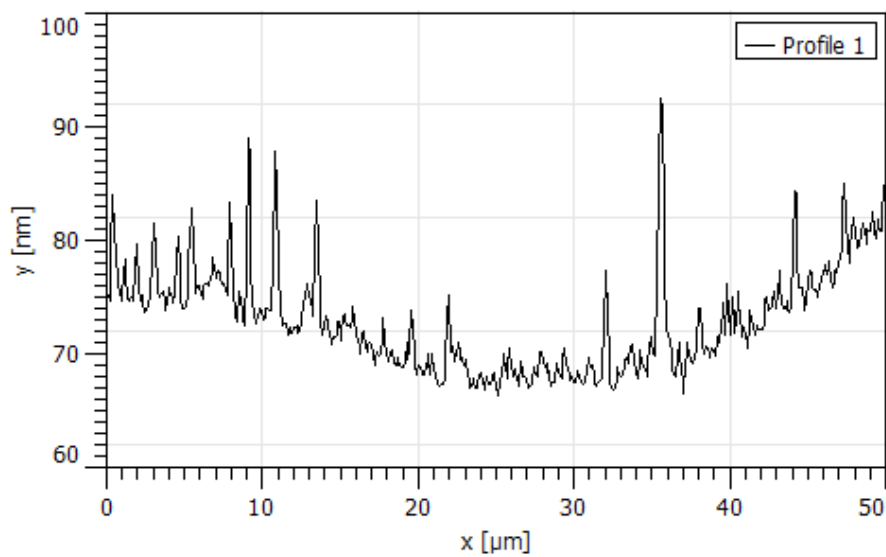


Figure2.26 Profile line for the substrate in Figure 2.25

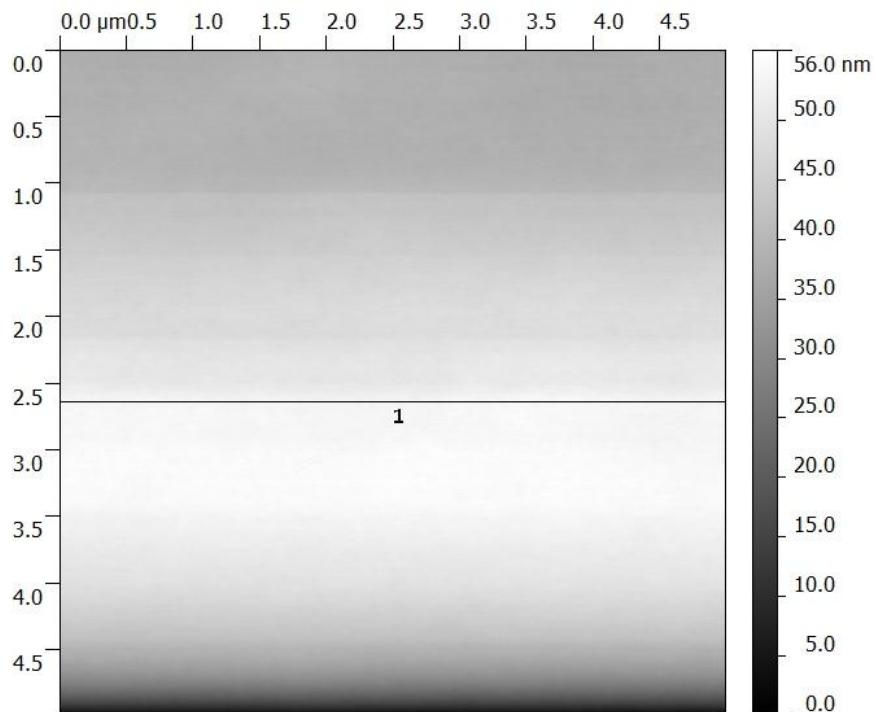


Figure 2.27 AFM image for the substrate cleaned up to hot methanol and exposed to gold for 24 hours

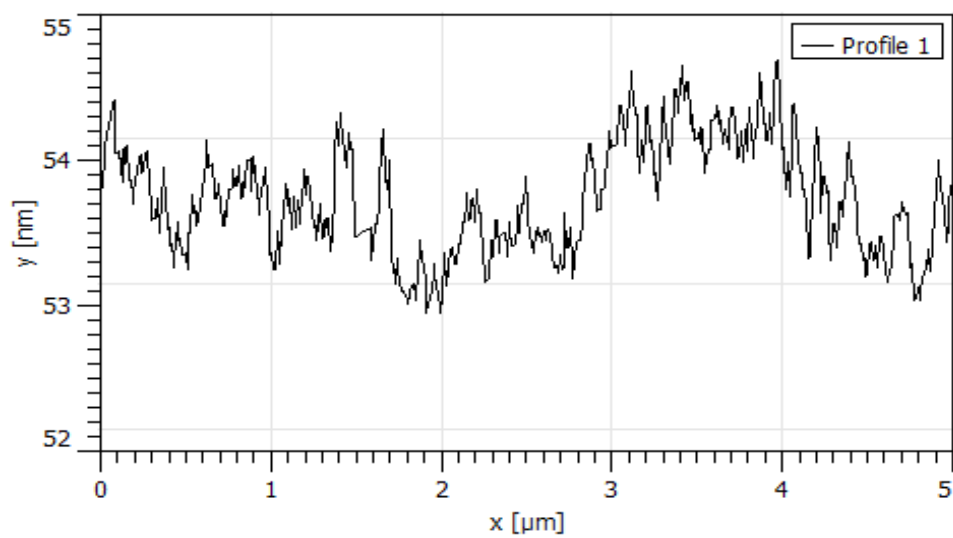


Figure 2.28 Profile line for the substrate in Figure 2.27

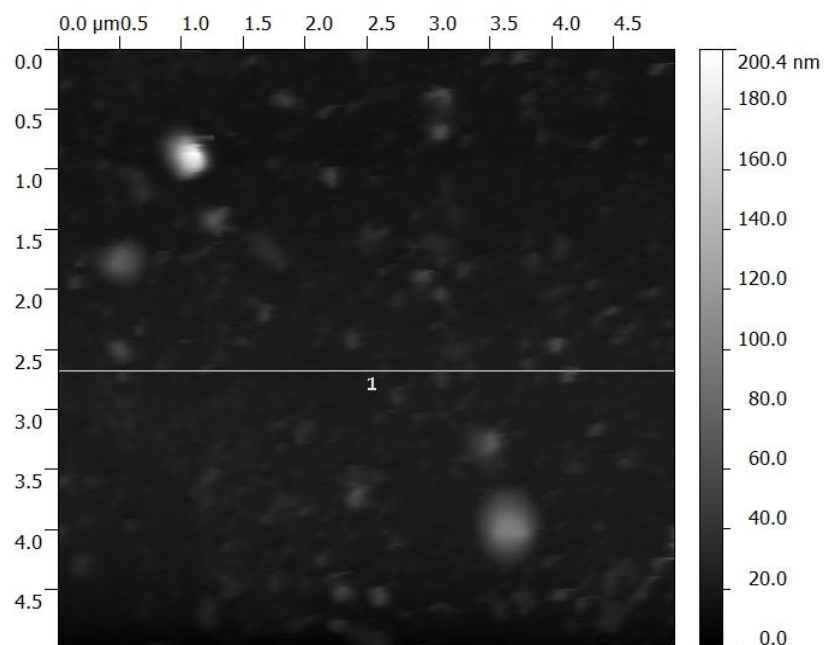


Figure 2.29 AFM image of PDDA stripes dried and exposed to gold

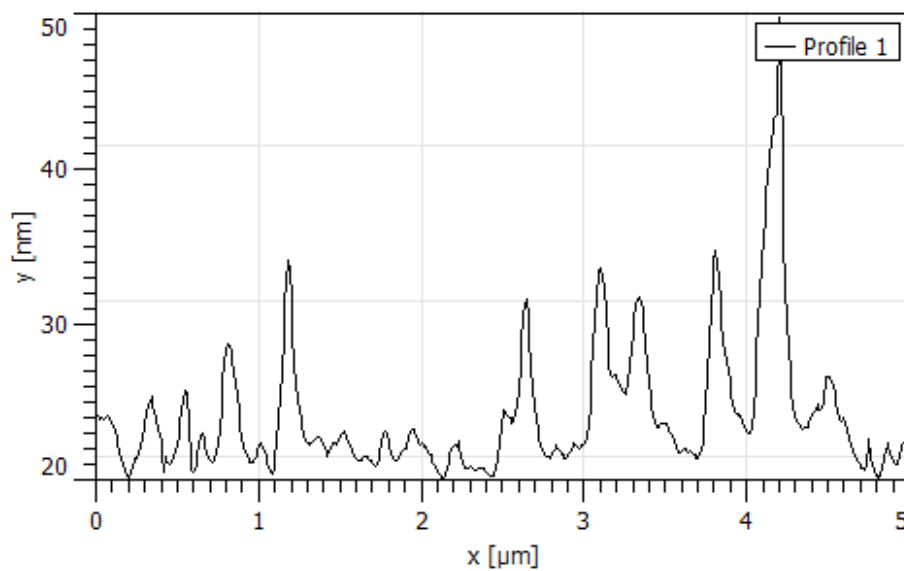


Figure 2.30 Profile line for the substrate in Figure 2.29

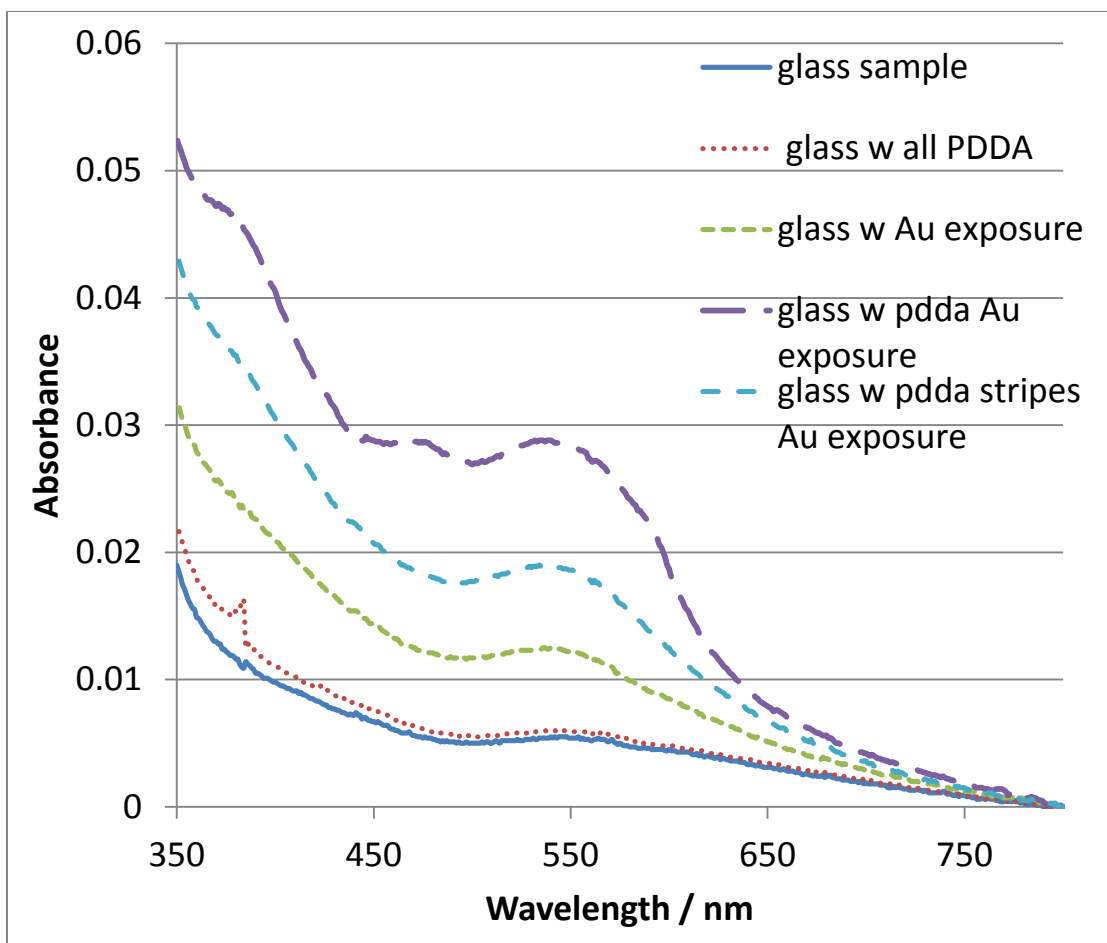


Figure 2.31 UV-visible spectroscopy of a series of substrates

ELECTROLESS DEPOSITION OF GOLD:

Electroless deposition of gold on substrates striped with 3:1 MMW PDDA from HAuCl_4 in the presence of the reducing reagent hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) was done using a spin vane for solution agitation for 30 minutes and without a spin vane (still solution) for 24 hours. Evidence of gold was found on both substrates, but was slightly more consistent when the spin vane was used. In both cases, the stripes were significantly affected as previously described. AFM images and

accompanying profile lines for the electroless deposition samples are shown in Figures 2.32 to 2.39.

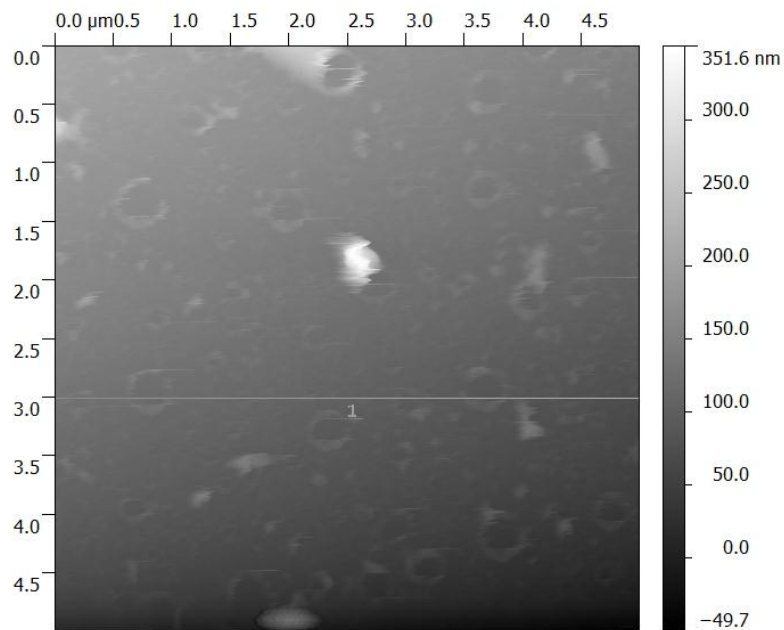


Figure 2.32 AFM image of electroless deposition done on substrate with spin vane

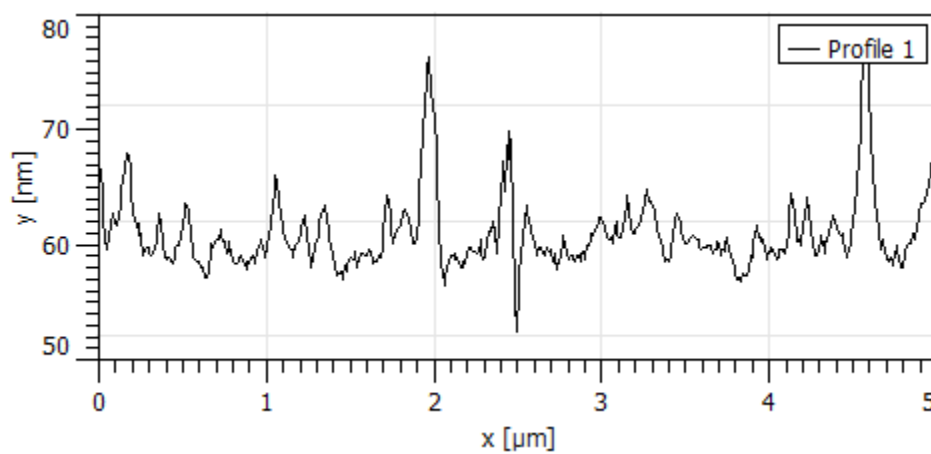


Figure 2.33 Profile line for the substrate in Figure 2.32

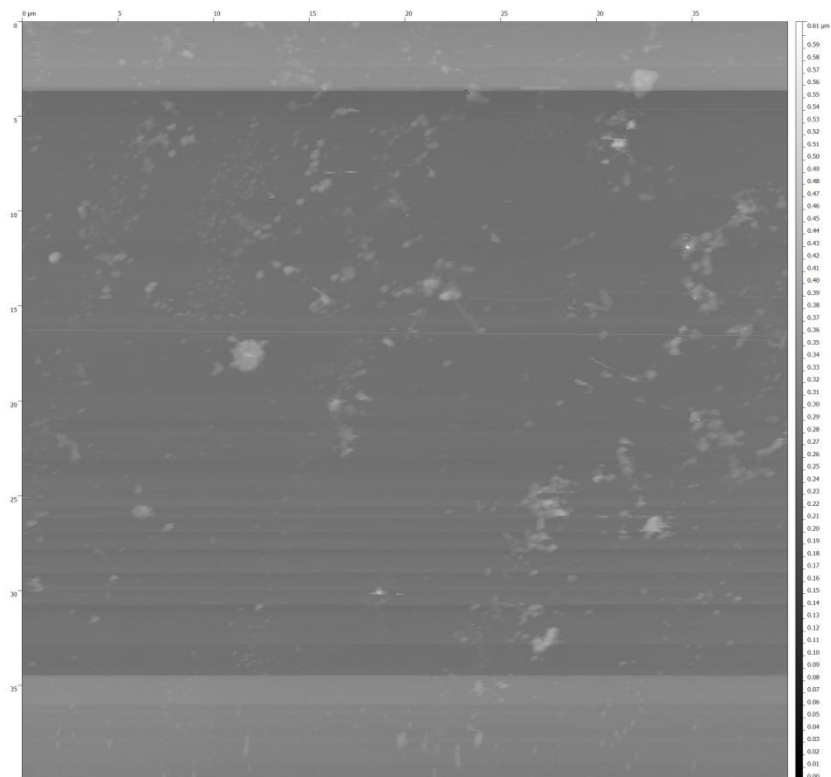


Figure 2.34 AFM image of substrate with electroless deposition

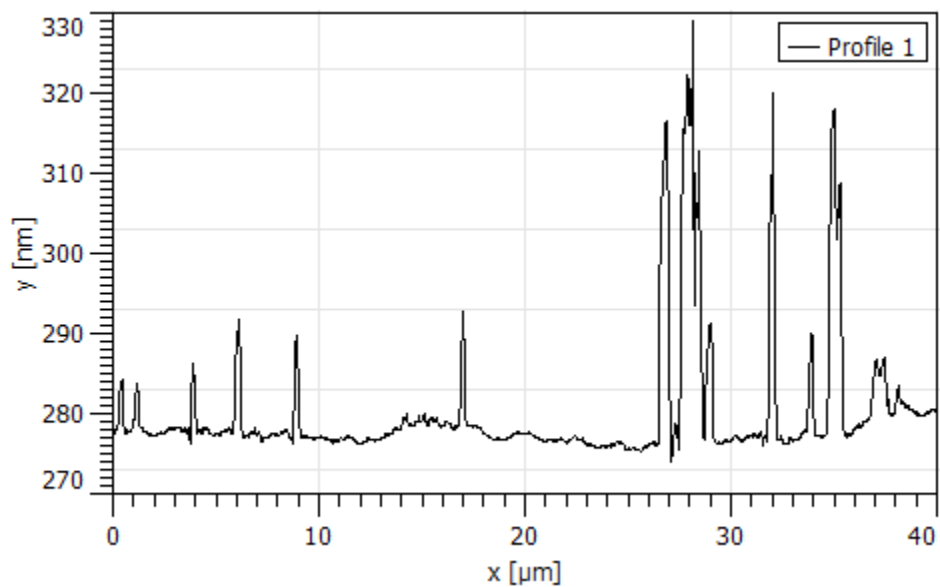


Figure 2.35 Profile line for the substrate in the Figure 2.34

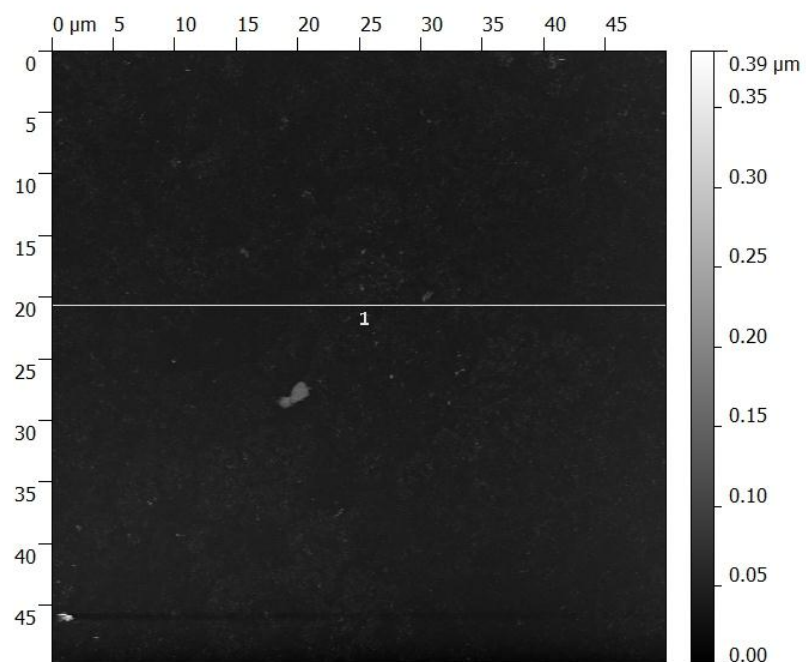


Figure 2.36 AFM image of substrate with electroless deposition without spin vane

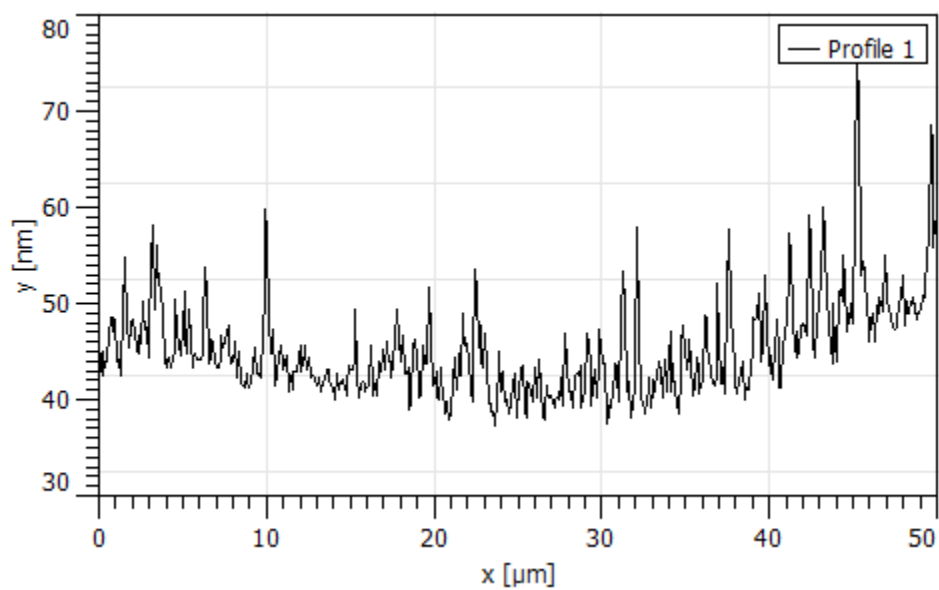


Figure 2.37 Profile line for the substrate in Figure 2.36

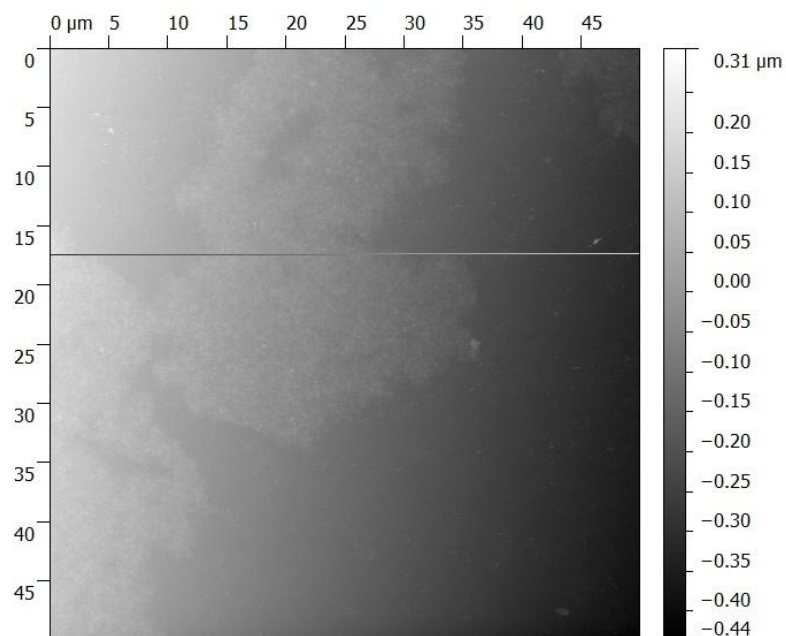


Figure 2.38 AFM image of substrate with electroless deposition without spin vane

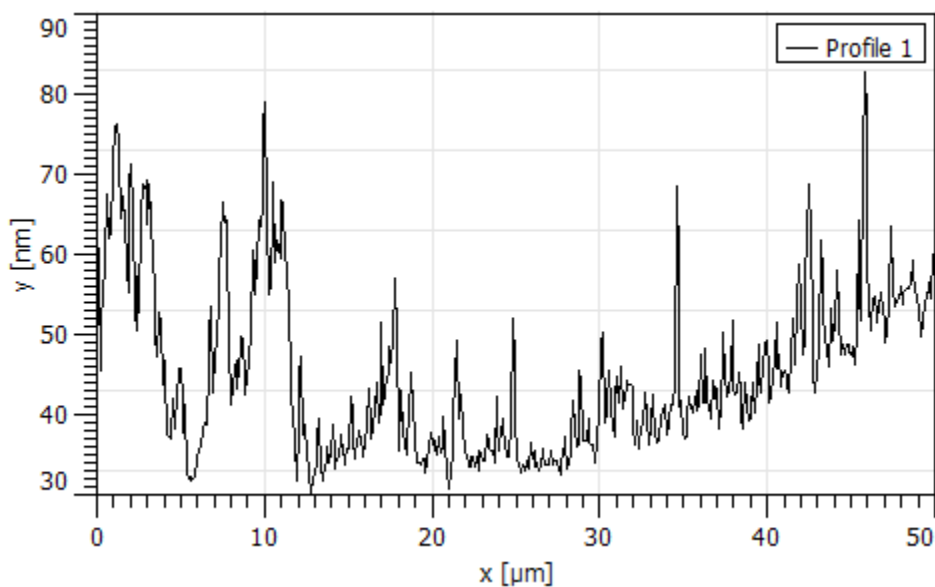


Figure 2.39 Profile line of the substrate for Figure 2.38

CONCLUSION

- To move forward from previous work where the entire glass substrate was coated with PDDA and fully coated with gold colloid, PDDA stripes were applied to the substrate. This was in hopes of creating electrically isolatable sensor platforms.
- PDDA stripes of 40 μm width or smaller were desired and were generally achieved by using a 1 mm capillary tube that was pulled to a much smaller diameter with a capillary puller. The best results were found with a 3:1 dilution of MMW PDDA.
- Exposure of the PDDA stripes to 5 nm gold colloid solution was attempted with mixed results. The binding of the gold nanoparticles was followed with UV-Visible spectrophotometer experiments and with the AFM images.
- The thickness of the PDDA stripes, which was 1 to 2 μm when initially applied, was reduced to a level not observable by the naked eye or under optical magnification levels. There was some slight evidence of PDDA remaining on the surface as shown by small amounts of adsorbed gold colloid. However, the concerted shape and location of the stripes was lost.
- Attempts at electroless deposition of gold solution onto 3:1 MMW PDDA stripes also showed little evidence of significant deposition of gold.

FUTURE WORK

In future work it is recommended that the following approaches be considered:

- Utilize a fully PDDA-coated substrate and apply stripes of gold colloid solution on that surface. This would give a more stable PDDA surface (~1.6 nm thick) that would be less likely to be lost or dissolved from the glass.
- Attempt to using ink-jet type printing technology to apply the gold colloid solution instead of pumping the solution with a device such as the PicoSpritzer.
- Investigate a different cationic polymer than PDDA that might be more tenaciously adsorbed onto the glass such as polymethyl methacrylate (PMMA) and polystyrene (PS) polymer.
- Attempt to add dye molecules to PDDA during dilution to help maintain visual reference for stripe location. However, there may be problems with dye reactivity.

BIBLIOGRAPHY

1. Wolfe, C.; Craver, B. P. Neutral particle lithography: a simple solution to Charge-related artifacts in ion beam proximity printing. *J. Phys.* **2008**, 41, 024007, p 12.
2. Xie, X. N.; Chung, H. J.; Sow, C. H.; Wee, A. T. S. Nanoscale materials Patterning and engineering by atomic force microscopy nanolithography *General Review* .**2006**, 54, p 1–48.
3. Kramer, S.; Fuierer, R.R.; Gorman, C. B. Scanning Probe Lithography Using Self-Assembled Monolayer's. *Chem. Rev.* **2003**, 103 (11), P4367–4418.
4. Madalina, C.; Dale, E. T. Glucose and Lactate Biosensors for Scanning Electrochemical Microscopy Imaging of Single Live Cells. *J. Anal. Chem.* 2008, 80, 2717-2727.
5. Zhao, Z.; Lei, W.; Wang, B.; Jiang, H. ZnO-Based Amperometric Enzyme Biosensors. *Sensors*. 2010, 10, 1216-1231.
6. Snow, E. S.; Campbell, P. M. Fabrication of Si nanostructures with an atomic force microscope. *Appl. Phys. Lett.* 1994, 64, 1932.
7. Hrapovic, S.; Liu, Y.; Enright, G.; Bensebaa, F.; Luong, J. H. T. New Strategy for Preparing Thin Gold Films on Modified Glass Surfaces by Electroless Deposition. *Langmuir* **2003**, 19, p 3958–3965.
8. Hou, Z.; Dante, S.; Abbott, N. L.; Stroeve, P. Self- Assembled Monolayer's on (111) Textured Electroless Gold. **1999**, 15 (8), P3011–3014.

9. Hidber, P.C.; Nealey, P. F.; Helbig, W.; Whitesides, G. M. New Strategy for Controlling the Size and Shape of Metallic Features Formed by Electroless Deposition of Copper: Micro contact printing of Catalysts on Oriented Polymers, Followed by Thermal Shrinkage". **1996**, 12 (21), p 5209–5215.
10. Meltzer, S.; Resch, R.; Koel, B.E.; Thompson, M. E.; Madhukar, A.; Requicha, A. A. G.; Will, P. Fabrication of Nanostructures by Hydroxylamine Seeding of Gold Nanoparticle Templates. **2001**, 17 (5), p 1713–1718.
11. Linford, M. R.; Chidsey, C. E. D. Alkyl monolayer's covalently bonded to silicon surfaces. *J. Am. Chem. Soc.* **1993**, 115 (26), p 12631–12632.
12. Whiteside, G. M.; Laibinis, P. E. Wet chemical approaches to the characterization of organic surfaces: self-assembled monolayers, wetting, and the Physical-organic chemistry of the solid-liquid interface. **1990**, 6 (1), p87–96.
13. Cappella, B.; Sturm, H. Comparison between dynamic plowing lithography and nanoindentation methods. *J Appl. Phys.* 2002, 91, 506.
14. Kotav, N.A.; Haraszti, T.; Turi, L.; Zavala, G.; Geer, R.E.; Dekany, I.; and Fendler, J.H. Mechanism of and Defect Formation in the Self-Assembly of Polymeric Polycation-Montmorillonite Ultrathin Films. *J. Am. Chem. Soc.* 1997, 119, 6821-6832.

