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CHEMICAL MODIFICATION ON GOLD SLIDES TO GAIN BETTER CONTROL OF PATTERNING TECHNIQUES

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

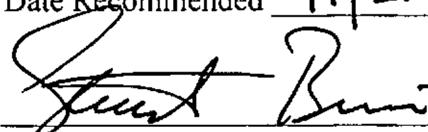
In Partial Fulfillment
Of the Requirements for the Degree
Master of Science

By
Ragini Vuppalapati

December 2011

CHEMICAL MODIFICATION ON GOLD SLIDES TO GAIN BETTER CONTROL OF PATTERNING TECHNIQUES

Date Recommended 11/22/2011



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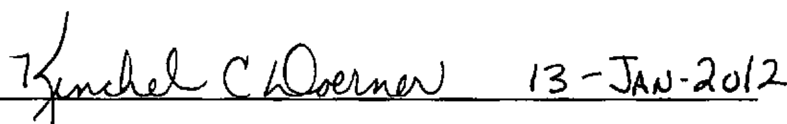

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Finally, I dedicate the thesis to my family, friends and to Dr. Burris who supported and encouraged me the most during my challenging times here at Western Kentucky University.

ACKNOWLEDGEMENTS

I wish to express my hearty thanks and appreciation for the contribution and help of many people who made this work possible, Dr. Stuart Burris for his everlasting support and patience, Dr. Darwin Dahl and Dr. Rajalingam Dakshinamurthy for their timely guidance and also for helping me write this thesis, members of my research group especially. I wish to thank Dr. Eric Conte for making me learn a lot in the field of Analytical Chemistry. I would like to express a deep sense of gratitude to Dr. Kevin Williams for his encouragement, I also wish to extend my gratitude to Dr. Bangbo Yan for his support, and guidance and help. I would like to thank Ms. Alicia McDaniel for her support and help. I owe special thanks to Dr. Stuart Burris who was involved in germination of this idea and also provided guidance and support till its completion. I would like to acknowledge Dr. Cathleen Webb for giving right advice in order to accomplish my goals.

I would also like to express my sincere gratitude and thanks to Ms. Shannon Marble and Ms. Aly Anderson for always helping me and making things easier and enjoyable.

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CHEMICAL MODIFICATION ON GOLD SLIDES TO GAIN BETTER CONTROL OF PATTERNING TECHNIQUES

Ragini Vuppalapati December 2011 92 Pages

Directed by: Dr. Stuart Burris, Dr.Kevin Williams and Dr.Rajalingam Dakshinamurthy

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Nanolithography is a rapidly evolving field that requires new combinations of techniques to improve patterning and to assist in fabricating electromechanical devices. An increasing number of applications require surfaces with defined regions of different chemical functionality. In our previous project optimum conditions for lithographic patterning were determined and potential blockers were identified to reduce force on the tip.

This work is focused on identifying good chemical modifications that will allow better control of basic patterning and to investigate the minimum force of patterning required while using each chemical system. The primary aim is to gain better control of basic pattern techniques in order to create more intricate patterns such as interdigitated arrays, which can subsequently be used in sensors. An atomic force microscope (AFM) is used to pattern the prepared colloid-coated glass slides. Several compounds were used in the investigation, including sodium sulphate, potassium sulphate, magnesium sulphate, sodium fluoride, sodium chloride, sodium bromide, and sodium iodide, potassium chloride, potassium bromide, potassium iodide, potassium dihydrogen phosphate, and potassium hydrogen phosphate.

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

- ✓ The groups of sulphates were determined to require minimum patterning forces as indicated.

  Sodium sulphate took a force of 49 n

  Potassium sulphate took a force of 45 nN

  Magnesium sulphate took a force of 744.4 nN

- ✓ The group of sodium and potassium halides were determined the minimum patterning forces as indicated.

  Sodium fluoride took a force of 8.42 nN

  Sodium chloride and potassium chloride took a force of 20.19 and 61.9nN

  Sodium bromide and potassium bromide took a force of 601.4 nN and 37.2 nN, respectively

  Sodium iodide and potassium iodide took a force of 953.7 nN and 47.2 nN, respectively

- ✓ The phosphates were determined to require the minimum patterning forces as indicated.

  Potassium hydrogen phosphate took a force of 25nN

  Potassium dihydrogen phosphate took a force of 43 nN

INTRODUCTION

Nanotechnology is involved in many processes that are important in the fabrication of integrated circuits, memory devices, display units, and biosensors. One of the important processes of nanofabrication is construction of functional units of size which are less than 100 nm. There are two new approaches of nanotechnology for the generation of nanostructures, one is top down and other is bottom up. The top down consists of various techniques that create the nanoscale patterns for a bulk material, where as the bottom down uses the interaction of molecules.[1]

The current and future developments in biotechnology and microelectronics require nanofabrication technologies of high spatial precision. The systems that are formed by manipulation of nanoparticulate level exhibit physical properties that are different from the properties of bulk materials. With the aid of the atomic force microscope, nanoparticles can be moved without the restrictions imposed by self-assembly methods.

The art of writing on a plate or stone with a completely smooth surface is known as lithography.[2] Nanolithography is a branch of nanotechnology that studies the fabrication of structures of approximately 100 nm.[3] Nanolithography has many techniques such as x-ray nano, scanning probe lithography, nano imprint lithography and atomic force microscope lithography. Among all these techniques AFM nanolithography is a unique tool for structure and patterning of materials with nanometer precision. In the early days of manipulation of nanoparticles, the 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 AFM. AFM is not only used to visualize the surfaces at molecular level but to modify surfaces as well. Gorman et al elaborated on various techniques and their advantages and disadvantages over each other for nanolithography. They explained various methods used for successful patterning.

Hrapovic etal fused gold nanoparticles on glass surfaces by electroless deposition where metal ions are reduced and deposited on the surface without applying an electrical potential.[4] Where a target surface is placed in plating bath solution which consists of complex metal ions and a reducing agent, the electroless deposition is favoured.[5-7] An ELD catalyst was used to deposit metals such as gold, copper, nickel, rhodium,[8] which can be used in formation of micro and nano scale metallic structures. The catalyst is used to reduce the metal ion only on the target surface area rather than the bulk solution. Electroless deposition allows the fabrication of printed circuits and hard disk memory.[9, 10]

The particles were reduced on the surface without applying any voltages. The gold particles were characterized by the AFM, cyclic voltametry and uv-vis spectroscopy to examine the morphology.[1] The gold nanoparticles are also fabricated on the glass surface by TEMPLATE STRIPPED TECHNIQUE.[11, 12] This technique was used to fabricate thin flat gold particles on the glass substrate. Specular x-ray reflectometry showed the solid films which are fabricated by this method were flat and had a good optical transparency, High stability, and good electrical conductivity. By using this technique, gold surface of 10 nm were produced which allows the optical transparency in the visible region and has a high stability and electronic conductivity. The gold nanoparticles which were prepared by electroless deposition were used in surface palsmon resonance spectroscopy (SPR), [13] which is used to characterize solid and liquid

interfaces and to study the interactions of biological molecules in optical sensors. To use this method we need to have very thin gold surfaces that can be prepared by electroless deposition, using this method the thickness of the films can be controlled on nanometer scale. The morphology and the roughness could be modified by tuning the size of the nanoparticles. A homogenous gold film at nano and sub nano surface was obtained.[14, 15]

EXPERIMENTAL

CHEMICALS: The gold particles were deposited on the glass surface by adsorption due to electrostatic attraction. Creating a surface with correct electrostatic environment.

The following chemicals and supplies were used:

NOCHROMIX: Concentrated sulphuric acid with a proprietary mixture of ammonium persulfate and detergents. This is used in place of piranha solution, as nochromix is safer to use and has a longer shelf life than piranha. It is a very strong oxidizer.[4]

ACS grade ETHANOL, ACS grade nitric acid

Type 1 deionized water which had a resistivity of greater that 16.7MΩ

Poly – (diallyammonium chloride) (PDDA) in four varieties

Very low molecular weight (<100,000g/mol)

Low molecular weight (100,000-200,000g/mol)

Medium molecular weight (200,000-350,000g/mol)

High molecular weight (400,000-500,000 g/mol)

Ultra High Purity Argon Gas (UHP Ar)-It is used to dry the substrate surface between cleaning steps and between layer assembly

Silanization solution: 5% Dimethyldichlorosilane in heptane

Gold colloid solution (5nm diameter)

Fisher brand microscope slide cover slips (12-543-C 22*50-2)

4-mL vials were used to contain the slides during and between most processing and preparation steps. Those used with gold colloid solutions were silicon zed to prevent the colloid particles from falling out of solution.

The atomic force microscope used in this study was a Molecular Imaging (Tempe, AZ) Pico Plus with a 100-µm XYZ closed –loop scanner and a Pico scan 3000 controller. MSCT AFM tips were purchased from Veeco Probes, Camarillo, CA.

A TIP - Force constant of 0.05n/m	D tip – Force constant of 0.03N/m
B tip – force constant of 0.02N/m	E tip – Force constant of 0.10N/m
C tip –force constant of 0.01N/m	F tip – force constant of 0.50N/m

Budget Sensors Multi -75 AFM tips were purchased from Nano and More USA, Lady's Island, SC.

SUBSTRATE PREPARATION

A microscopic cover slip (50 × 24 × 0.22 mm) scored it into seven equal sections, taking care that the cover slip does not break. The slip was degreased by exposure to ethanol vapor for 2 hours in Soxhlet extractor.[4] It was then snapped into pieces, each 2.4 cm long and approximately 7 mm wide. These smaller substrates were then placed in 50% nitric acid for 30 minutes. This treatment was followed by washing with Type I deionized water. The substrates were then immersed in freshly prepared Nochromix™ solution for 45 minutes. Nochromix treatment was substituted for hot piranha solution (70:30 conc.H_2SO_4:30%H_2O_2) because Nochromix is much safer and has a longer shelf life than piranha. The Nochromix treatment was followed by washing with Type I deionized water. The substrates were further rinsed with methanol and hot Type I deionized water and then dried under stream of ultra high purity argon gas (UHPAr). This procedure removes any organic contamination from the slide and maximizes the exposure

of negatively charged Si OH groups on the surface of the slide, which facilitates the adhesion of the polymer layer to the slide by allowing for greater interaction between the Si OH groups on the slide and the quartnery ammonium groups in the polymer.[1]

This substrate is then placed in medium molecular weight poly (diallydimethylammoniumchloride), PDDA, solution for 120 minutes. After the adsorption of the PDDA, the slide is then rinsed in Type I deionized water and dried using a stream of UHP Ar. From this point, substrates were soaked for one hour in a 1.0 M solution of an ionic compound intended to modify the interaction between the PDDA and the gold colloid. After being rinsed with Type I deionized water, the substrates were then incubated in gold colloid solution (5 nm diameter) for 24 hours. They are then rinsed with Type I deionized water and stored in a glass vial until they are scanned and/or modified using an atomic force microscope.

Salts and other compounds being investigated include sodium sulphate, potassium sulphate, magnesium sulphate, potassium chloride, potassium bromide, potassium iodide, sodium fluoride, sodium chloride, sodium bromide, sodium iodide, phosphoric acid, potassium dihydrogen phosphate, potassium hydrogen phosphate, and sodium phosphate.

The prepared substrates are patterned using an atomic force microscope (AFM). The substrate is initially imaged in contact mode using a very light force. The images produced are used to choose a suitable area to pattern. The software used to control the patterning process is called PicoLITH. This program allows a wide range of shapes to be patterned onto the sample surface. A number of different patterning forces can be used in each pattern, if desired, by associating different forces with different colors. The target is to create a systematic pattern such as an interdigitated array.

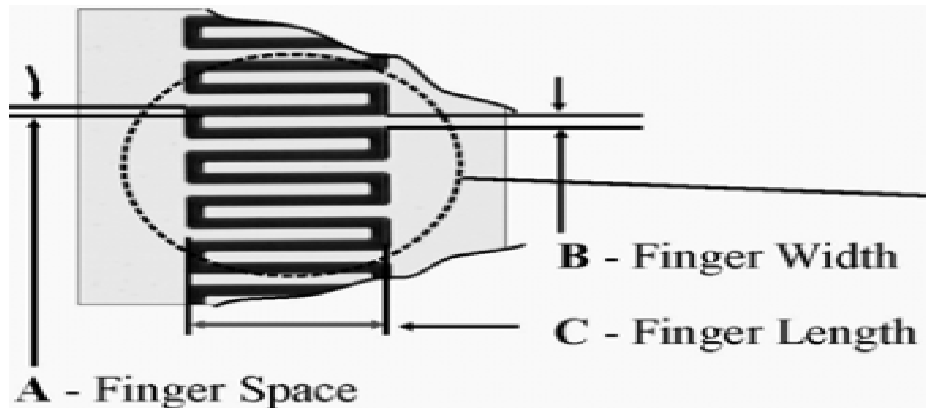

Figure 1: Interdigitated array illustration [17]

Typical finger widths and finger spaces are 100nm and the length is typically 5-10 µm. The force required to pattern is then calculated by measuring the force constant of the tip, the deflection sensitivity of the tip, and the amount of tip deflection.

By using the Thermal K accessory on the AFM, the force constant of an AFM probe can be calculated. As part of the force constant measurement, the deflection sensitivity is calculated by collecting a “force curve” or deflection curve – a plot of force or cantilever deflection versus distance from the substrate. A steep portion of deflection curve is taken to calculate the deflection sensitivity in nm per volt. Various parameters like acquisition time, average cantilever shape and correct ambient temperature in Celsius are input to the program before calculating the spring constant. This force is applied to the tip and the surface is patterned. After the patterning is done, the deflection sensitivity is taken to calculate the actual force the tip used to pattern the surface.

FOR EXAMPLE: POTASSIUM SULPHATE

The deflection was at	6.0 V
The Deflection sensitivity	55.848 nm/V
Force Constant	0.135 nN/nm

FORCE = Deflection × Deflection sensitivity × Force Constant

FORCE = 6.0 V × 55.848 nm/V × 0.135 nN/nm = 45 nN

QUANTIFYING THE FORCES REQUIRED FOR PATTERNING

Measuring the force constant of each individual tip that is used to pattern the slide, and with it the minimum force required to pattern while using each potential blocker, the modifying effect was quantitatively investigated.

Several compounds were used in the investigation, including sodium sulphate, potassium sulphate, magnesium sulphate, sodium fluoride, sodium chloride, sodium bromide, sodium iodide, potassium chloride, potassium bromide, potassium iodide, potassium dihydrogen phosphate, and potassium hydrogen phosphate.

The force of the tip was measured by taking 2 or more sweeps of the tip, measuring the deflection sensitivity and force constant of the tip. As various tips were being used like the E tip which had a force constant of ~0.01 N/m, the F tip which had a force of ~0.1 N/m and the Multi -75 tip which had a spring constant of ~3 N/m. The forces of these tips were measured when the patterning was done each time.

The images of the prepared slides were obtained by using the atomic force microscope in imaging mode. 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. Below are the two different types of pattern.

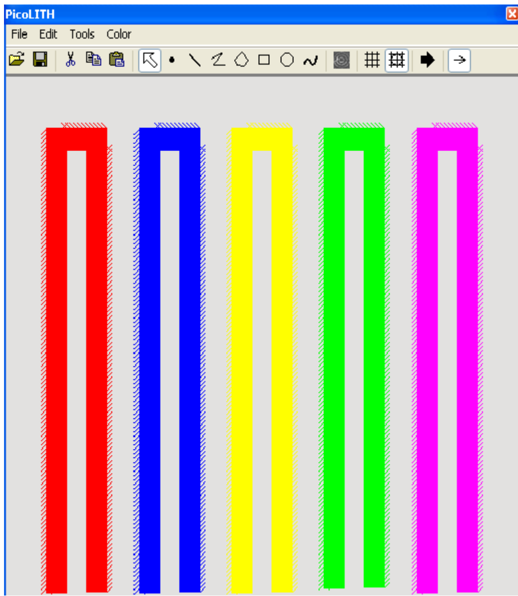

Figure 1.1 Pico lith image of Line bar pattern

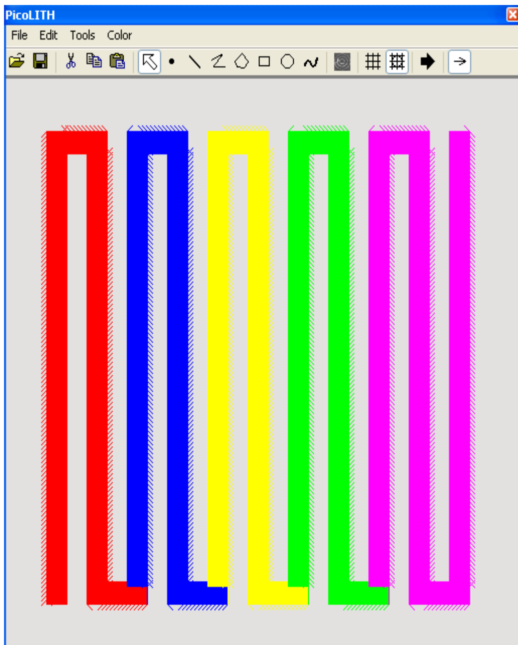

Figure 1.2: Pico lith image of interdigitated array pattern

The chemical modifications which would change the required force for patterning and to quantitatively investigate the force of patterning equal to force of chemical system ($f_{patterning} = f_{chemical\ system}$).

RESULTS AND DISCUSSION

Determining the force required for patterning

With the goal of finding out the required force for patterning, the force required for patterning each compound and the force of the tip used was measured.

SULPHATE SERIES:

SODIUM SULPHATE. The sodium sulphate was first tried with the E tip at various set points, the line bar and the interdigitated pattern.

E –TIP

SET POINT 1.0 V: When the set point 1.0 was applied and tried to pattern with the e tip there was no patterning seen , there were only the distribution of the colloid particles as seen in Figure 3.1.

SET POINT 2.0 V: With the set point of 2.0 there was uniform distribution of the particles as seen in Figure 3.2.

SET POINT 2.4 V. At this set point the line bar pattern, was imaged which was not clear as seen in Figure 3.3.

SET POINT 3.4 V: A partly patterned line bar was imaged; therefore this force was not enough to pattern the sodium sulphate as seen in Figure 3.4.

SET POINT 3.6 V: So the set point was further raised to 3.6 and patterned. The image had the last two lines of the line bar pattern were being partly patterned as seen in Figure 3.5.

SET POINT 3.8 V: Patterned at a higher set point and when the pattern was imaged, the last line which was at set point 4.6 was patterned as seen in Figure 3.6.

SET POINT 4.8 V: The last line at 4.6 was patterned the set point was further raised the 4.8 and tried to pattern when imaged the pattern all the lines were partly patterned as seen in Figure 3.7.

SET POINT 5.8 V: In order to get a very clear patterned image the set point was further more raised to 5.8 and patterned it with line bar. All the lines were clearly patterned as seen in Figure 3.8.

SET POINT 7.6 V: When a profile was taken of the image at 5.8 it was observed that the patterning was not 5 nm deep as the gold particles size used to adsorb on the glass slide were 5 nm. Therefore, the set point further raised and patterned with interdigitated, a clear image was obtained where all the particles were swept in the interdigitated pattern, as seen in Figure 3.9 and the force required to pattern was 49 nN. Figure 3.10 shows the profile line of the patterned area.

POTASSIUM SULPHATE

SETPOINT 2.0 V: The potassium sulphate was patterned with the E tip where a force of 2 V was applied there was not much patterning at this force where only the last line of the line bar was patterned as seen in Figure 3.11.

SET POINT 3.0 V: With the force of 3 V all the lines were patterned, but the particles were not completely swept as seen in Figure 3.12.

SETPOINT 4.0 V: When the force was increased to 4 V the particles were not swept clearly, which states the force was not sufficient to sweep the particles as seen in Figure 3.13.

SET POINT 5.0 V: At this force the particles were partly swept, this force was not sufficient to completely sweep the particles. This resulted in partly patterned image as seen in Figure 3.14.

SET POINT 6.0 V: The force was further more raised to 6 V, the particles were clearly swept the lines were clear as seen in Figure 3.15; the same force was applied to another pattern leave a bar as seen in Figure 3.16. The profile line of the patterned image is shown in Figure 3.17. The force required to pattern the potassium sulphate was 45 nN.

MAGNESIUM SULPHATE: The force required force to pattern the magnesium sulphate was tried with the E tip which had a force of 0.01N/m.

E-TIP:

SET POINT 2.0: The force of 2 V was applied to the magnesium sulphate slide; six rectangles were tried to pattern at this force. After a 45 minute scan when the sample was imaged, there was no change, the uniform distribution of the colloid particles were imaged as seen in Figure 3.18.

SETPOINT 3.0: The force from 3 V to 4 V were applied to the six rectangles and swept across the sample by using the E tip. After a 45 minute scan there was no patterning observed on the sample as seen in Figure 3.19.

SETPOINT 4.0: The force was increased to 4 V and tried to pattern on the magnesium sulphate sample, there was no patterning seen and the image has the colloid particles as seen in Figure 3.20.

SET POINT 5.0: The next higher force of 5 V was applied to the six rectangles and tried to pattern at this force, but when the sample was imaged, the rectangles were being partly patterned as seen in Figure 3.21.

SET POINT 6.0: With the force of 6 V all the rectangles were being partly imaged at the force of 6.2 V and 6.3 V the particles were partly swept in the rectangular pattern as seen in Figure 3.22.

There was no patterning seen with the E TIP even at a higher force of 6 V hence a higher force tip was used. The F tip was used which has a force of 0.1 N/m.

SET POINT 0.8 V: At this Force all the bars were patterned, but the grooves were not 5 nm deep because there were no particles on the slide, Hence it took very less force to pattern as seen in Figure 3.23.

SET POINT 4.5 AND 5.4 V: At these forces the particles were patterned but the 100 nm width of the interdigitated pattern was not achieved as seen in Figures 3.24 and 3.25.

SET POINT 6.3V: At this force there was a partly patterned image of the magnesium sulphate as seen in Figure 3.26.

SET POINT 7.0 7.2, 7.9 and 8.9 V: At these forces the magnesium sulphate was partly patterned as seen in Figures 3.27, 3.28, 3.29, and 3.30.

As there was no patterning seen even on the F tip the magnesium sulphate was tried to pattern through Multi -75 tip which has s force constant of 3N/m.

SET POINTS 2.0, 3.0, 4.0 and 5.0 V: At these forces all the bars were patterned the particles were swept partly as seen in Figure 3.31, 3.32, 3.33, and 3.34.

SET POINT 5.9 V: At this set point all the particles were patterned and the grooves were 5 nm deep as seen in Figure 3.35 and in the profile line of patterned area in Figure 3.36. The force required to pattern magnesium sulphate is 744.4 nN.

Figure 3.37 is a spreadsheet showing the relation between the compound and the amount of force it took to get patterned.

Figure 3.38 shows a relation between the force the compound and its ionic radius.

Figure 3.39 shows a relation between the force and charge/ionic radius.

HALIDES SERIES

In the halide series the sodium halides were first prepared and the force required to pattern these halides were investigated by using the E TIP.

SODIUM FLUORIDE:

The sodium fluoride was the first halide; it was tried to pattern using the E TIP.

SET POINT 1.0 V: When the force of 1 V was applied to the sodium fluoride slide it was observed that the particles were swept completely and the sodium fluoride was patterned on leave a bar as seen in Figure 3.40. This pattern has more number of lines in 119 nN. The profile line of the patterned sodium fluoride is shown in Figure 3.41.

SODIUM CHLORIDE

SET POINT 0.8 V: At a force of 0.8 V there was not much patterning done on the sample as seen in the Figure 3.42, partly imaged leave a bar was observed; therefore, this force is not sufficient to pattern the sodium chloride.

SET POINT 1.0 V: At a force of 1 V the particles were partly swept and the pattern could be much clearly seen in Figure 3.43 in contrast to the force applied at 0.8V, but when the profile was taken the particles were not patterned 5 nm deep, therefore this force is not sufficient to pattern the sodium chloride.

SET POINT 1.9 V: Interdigitated pattern was used at this force, starting from 1.9-2.3 V was applied and it was observed that all the particles were completely swept and a clear image was obtained as seen in Figure 3.44. The force required to pattern the sodium chloride was 167 nN. The profile line of the patterned area is seen in Figure 3.45.

SODIUM BROMIDE

E tip was used to pattern the sodium bromide

SET POINT -0.3 V: When this force was applied to the leave a bar pattern, only the bar with a force of -0.3 V was being patterned as seen in Figure 3.46. Therefore, this force is not sufficient to pattern Sodium bromide

SET POINT 1.0 V: When a force of 1.0, 1.5, 2.0, 2.5, and 3.0 V, were applied to each bar and after a 150 minute scan it was observed that only the first three bars at the force of 1.0, 1.5, 2.0 V were being patterned as seen in the Figure 3.47. Therefore 2.5 and 3.0 V force was not sufficient to pattern the sodium bromide.

SET POINT 2.2 V: When a force of 2.2, 2.7, 3.2, 3.7, and 4.2 V were applied to each bar after a 150 minute scan it was observed that 2.2V force was patterned, 3.2, 3.7, 4.2 V were partly patterned and at the force of 2.7 V there was no patterning seen as seen in Figure 3.48. There was no uniform patterning observed at this force. Therefore, this force is not sufficient to pattern the sodium bromide.

SET POINT 3.7 V: At this force all the bars were partly patterned, the particles were not swept completely as seen in Figure 3.49. In the bar pattern one part of the bar was patterned and the other part was partly patterned. Therefore, this force is not sufficient to pattern the sodium bromide.

SET POINT 4.7 V: When a force of 4.7, 5.2, 5.7, 6.2, and 6.7 V, was applied to the bars it was observed that at 5.7 V the bar was not patterned as seen in Figure 3.50. The particles at the force of 4.7, 5.2, 6.2, and 6.7 V were swept, but there was no uniform patterning on the sample. Therefore this force is not sufficient to pattern the sodium bromide.

SETPOINT 5.2 V: The force was further increased to 5.2, 5.7, 6.2, 6.7, and 7.2 V, similar patterning was observed as seen at 4.7 V, where 6.2 was not patterned and 5.2, 5.7, 6.7, and 7.2 were partly patterned as seen in Figure 3.51. The particles were not swept uniformly; therefore, this force is not sufficient to pattern the sodium bromide.

SET POINT 6.2 V: At this force all the bars were partly patterned there was no complete sweeping of the particles as seen in Figure 3.52. Therefore this force is not sufficient to pattern the sodium bromide.

As there was no patterning seen with the E TIP the sodium bromide was patterned using the next higher force, the F TIP which has a force of 0.1N/m, a higher force was applied to the sodium bromide in order to pattern it.

F TIP:

SET POINT 0.1 V: A lesser force of 0.1 V was applied to the sodium bromide on the F TIP and after a 150 minute scan it was observed that the force was not sufficient as the

particles were not swept and there was not enough patterning done on the sample, as seen in the Figure 3.53; therefore, this force is not sufficient to pattern the sodium bromide.

SET POINT 3.2 V: When the force of 3.2, 3.7, 4.2, 4.7, and 5.2V was applied, at the force of 3.7V the particles were swept as seen in Figure 3.54 the bars with the force of 3.2, 4.2, 4.7, 5.2 V was not clearly patterned, therefore this force is not sufficient to pattern the sodium bromide.

SET POINT 5.2 V: The force was increases to 5.2 V in order to see a better patterning, but when the sample was tried to pattern, the particles were not swept and force was not sufficient to pattern because the particles were not deep enough as seen in Figure 3.55.

SETPOINT 5.4 V: When a series of forces were applied starting from 5.4, 5.5, 5.8, 6.1, 6.4 V, at the force of 5.4 V there was no patterning on the sample as seen in Figure 3.56 the rest of the bars were patterned, but the force was not sufficient to achieve the width of 100 nm as originally used for the bars.

SET POINT 5.8 V: When the force was increased to 5.8, 6.1, 6.4, 6.7, and 7.0 V, the bars with the force of 5.8 and 6.4 V were clearly patterned as seen in Figure 3.57, the rest of the bars were not patterned because the force was not sufficient to pattern.

SET POINT 7.0 V: At this force the first bar at 7.0 V was patterned. As seen in Figure 3.58.

With the F tip there was no patterning seen on the sodium bromide. Hence, the force of the F tip is not sufficient to pattern the sodium bromide, so a higher force tip of Multi-75 was used which has a force constant of 3 N/m.

MULTI-75 TIP:

SET POINT -0.3 V: Force of -0.3, 0.2, 0.7, 1.2, and 1.7 V was applied and patterned, as seen in the Figure 3.59, the bar at the force of 1.7 V was being patterned, because the rest of the forces were not enough to pattern.

SETPOINT 2.9: As the bar at 1.7 V was patterned, the force was raised to 2.9 V and tried to pattern, as seen in Figure 3.60; the bar at the force of 2.9 V was patterned.

SET POINT 3.8: At this force all of the bars were patterned, but the grooves were not 5 nm deep and the width of the bars also were not 100 nm as seen in Figure 3.61. Hence this force is not sufficient to pattern the sodium bromide.

SETPOINT 5.9: The force was raised to 5.9 V and patterned as seen in Figure 3.62, all of the bars were clearly patterned as seen in the profile line in Figure 3.63 the grooves were 5 nm deep and the particles were completely swept. The force required to pattern sodium bromide was 601 nN.

SODIUM IODIDE:

MULTI 75 TIP:

SET POINT 3.0 V: At this force there was no patterning done as seen in Figure 3.64.

SET POINT 3.1, 3.6, 4.2 V: At these three forces the sodium iodide was patterned but the grooves of the bars were not 5 nm deep and chosen 100 nm width of the interdigitated pattern was not achieved as seen in Figures 3.65, 3.66, 3.67. Hence these forces are not sufficient to pattern the sodium iodide.

SET POINT 4.5 V: When forces of 4.5, 4.6, 4.7, 4.8, 4.9 V were being applied to the individual bars of the interdigitated pattern and imaged only the first three forces i.e 4.5,

4.6, 4.7V are being patterned as seen in Figure 3.68. Hence these forces are not sufficient to pattern the sodium iodide.

SET POINTS 4.8, 5.3, 5.7, 6.3, 7.0, 8.5, 9.0: At these forces the sodium iodide was partly patterned and the grooves of the bars were not 5 nm deep and chosen 100 nm width of the interdigitated pattern was not achieved as seen in Figures 3.69, 3.70, 3.71, 3.72, 3.73, 3.74, 3.75. Hence these forces are not sufficient to pattern the sodium iodide. Figure 3.76 shows the profile line of the patterned area.

Sodium iodide need much more force to get patterned as it was not patterned with multi 75 tip.

Figure 3.77 and 3.78: Is the graph which shows the relation between force took by the compound and the relation between force and ionic radius of the compound.

Figure 3.79: Is the graph showing the relation between the force and the charge/ionic radius.

POTASSIUM SERIES: In the potassium series, the force required to pattern potassium chloride, potassium bromide and potassium iodide was investigated.

POTASSIUM CHLORIDE:

E TIP:

SETPOINT 2.0 V: potassium chloride was tried to pattern with the E TIP at a force of 2.0V, as seen in Figure 3.80, there was distribution of particles and no patterning done.

SET POINT 3.0 V: At this force all of the bars were partly patterned as seen in Figure 3.81.

SET POINT 4.0 V: The line bar pattern was used and a series of forces from 3.0, 3.2, 3.4, 3.6, 3.8, 4.0 V. As seen in Figure 3.82, the bars at the first two forces 3.0 and 3.2 V were not being patterned, as the force was less to pattern potassium chloride.

SETPOINT 6.0 V: At this force all bars were patterned but the grooves of the bars were not 5 nm deep as seen in the image Figure 3.83.

SETPOINT 7.0 V: At this force all of the bars were patterned as seen in Figure 3.84 and the grooves were 5 nm deep as seen in the profile image of Figure 3.85, and the particles were completely swept .The force required to pattern potassium chloride is 61.9 nN.

POTASSIUM BROMIDE

E TIP: potassium bromide was patterned using the E TIP.

SETPOINT 2.0 V: At this force all the bars were unevenly patterned as seen in Figure 3.86.

SETPOINT 3.0 V: When a series of forces are applied to line bar pattern, from 3.0, 3.2, 3.4, 3.6, 3.8, 4.0 V. The bars with the force of 3.4, 3.6, 3.8, 4.0 V were being patterned as seen in Figure 3.87.

SET POINT 4.0 V: At this force the bars were patterned but were not 5 nm deep as seen in Figure 3.88

SET POINT 4.5 V: Patterning was achieved at this force were the particles were swept, as seen in Figure 3.89, and the grooves were 5 nm deep as seen in the profile line in Figure 3.90. The force required to pattern potassium bromide was 37.2 nN.

POTASSIUM IODIDE:

E TIP:

SET POINT 0.6 V: At this force the last bar with a force of 1.0 V was being patterned as seen in the image 3.91.

SET POINT 1.6 V: At this force all the bars were not patterned, as seen in the image Figure 3.92.

SET POINT 2.6: At this force only two bars were patterned with the force of 2.6and 2.7 V. As seen in the Figure 3.93.

SET POINT 3.8: At this force the first three bars were patterned as seen in the Figure 3.94.

SET POINT 4.0.V: At this force the last three bars were being patterned as seen in Figure 3.95.

SET POINT 5.0 V: all the bars except the last bar with the force of 5.4V were not patterned as seen in Figure 3.96.

SET POINT 6.0: At this force there was clear patterning seen all the particles were swept as seen in Figure 3.97, the potassium bromide was patterned with the E tip and the grooves were 5 nm deep as seen in the profile line of Figure 3.98.

Figure 3.99 and 4.00: Shows a relation between the force the compound took to get patterned and the force and ionic radius of the potassium series.

Figure 4.1: Shows a relation between the force and the charge/ionic radius.

PHOSPHATE SERIES: In the Phosphate series two phosphates which are potassium hydrogen phosphate and potassium dihydrogen phosphate were taken and the force required to pattern these phosphates was investigated.

POTASSIUM HYDROGEN PHOSPHATE:

E TIP:

SET POINT -0.3, 2.0, 2.1, 2.9, and 3.0: potassium hydrogen phosphate was tried to pattern at these forces on e tip, as seen in Figures 4.2, 4.3, 4.4, 4.5, and 4.6. The patterning done was not uniform, the grooves of the leave a bar was not 5 nm deep and particles were not swept, so these forces are not sufficient to pattern potassium hydrogen phosphate.

SET POINT 3.5: At this force the particles were completely swept as seen in Figure 4.7 and the grooves were 5 nm deep as seen in profile line in Figure 4.8. The force required to pattern potassium hydrogen phosphate is 25 nN.

POTASSIUM DIHYDROGEN PHOSPHATE:

E TIP: potassium dihydrogen phosphate was tried to pattern with the E TIP.

SET POINT 1.0 V: At this force the lines were being partly patterned, as this force was not sufficient for it to sweep the particles and pattern it as seen in Figure 4.9.

SET POINT 2.0 V: With different forces applied to the bars, the bar at the force of 2.0 V was patterned as seen in Figure 4.10.

SET POINT 3.0 V: When the forces of 3.0, 3.1, 3.2, 3.3, and 3.4 V were applied to the bars, the bars at the force of 3.0 and 3.2V were partly patterned as seen in Figure 4.11.

SET POINT 4.0 V: At this force the first two bars 4.0and 4.1 V were patterned as seen in Figure 4.12.

SET POINT 5.0 V: At this force there was some impressions of the leave a bar pattern on the sample but it was not patterned as seen in Figure 4.13, hence this force is not sufficient to pattern the phosphate.

SET POINT 6.0 V: At this force the particles were not swept at force of 6.0, 6.1 and 6.2 V, whereas the particles at the force of 6.3 and 6.4 V were being patterned as seen in Figure 4.14.

F TIP: As there was no patterning achieved with E tip potassium dihydrogen phosphate was tried to pattern through the F TIP.

SET POINT 2.0 and 2.5 V: This force was not sufficient to sweep the particles as the bars with the force of 2.0 V and at 2.5 V were patterned as seen in Figures 4.15 and 4.16.

SET POINT 3.0: all the bars were patterned, but the grooves of the bars were not 5 nm deep as seen in Figure 4.17.

SET POINT 3.5: At this force all the particles were patterned as seen in Figure 4.18 and the particles were 5 nm deep as seen in Figure 4.19. The force required to pattern the potassium dihyrogen phosphate is 43 nN.

Figure 4.20: Shows the relation between the force the phosphates took to get patterned.

Figure 4.21: Shows the relation between the force and the charge/radius ratio.

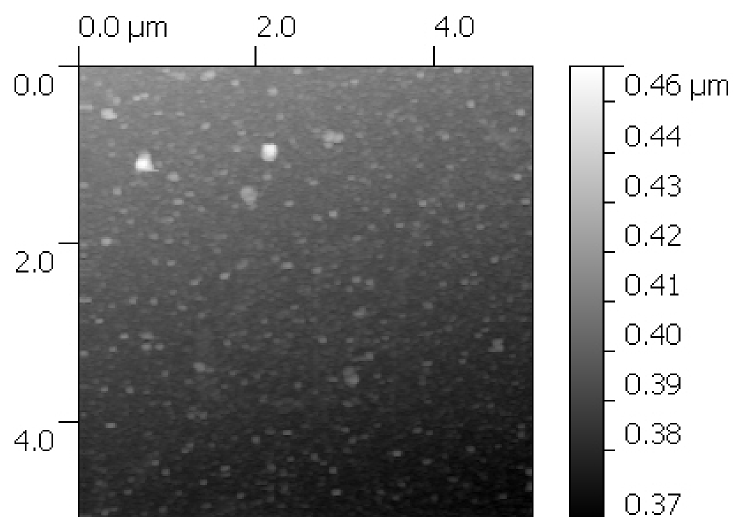

Figure 3.1 AFM image of sodium sulphate at a set point of 1.0V

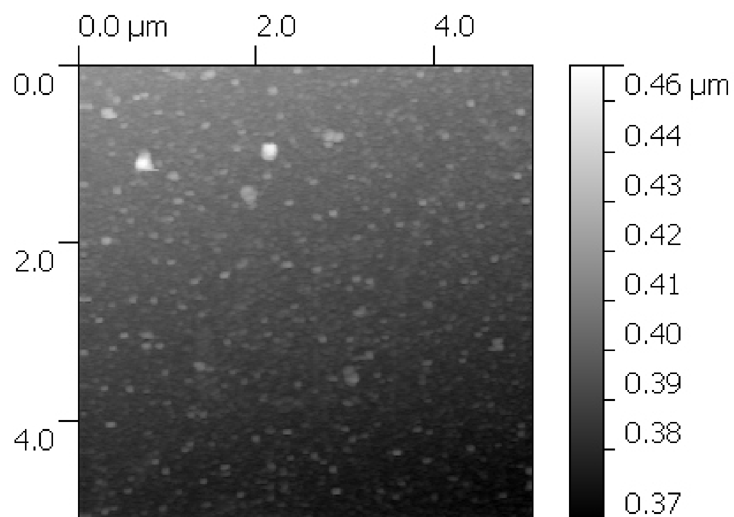

Figure 3.2 AFM image of sodium sulphate at set point of 2.0V

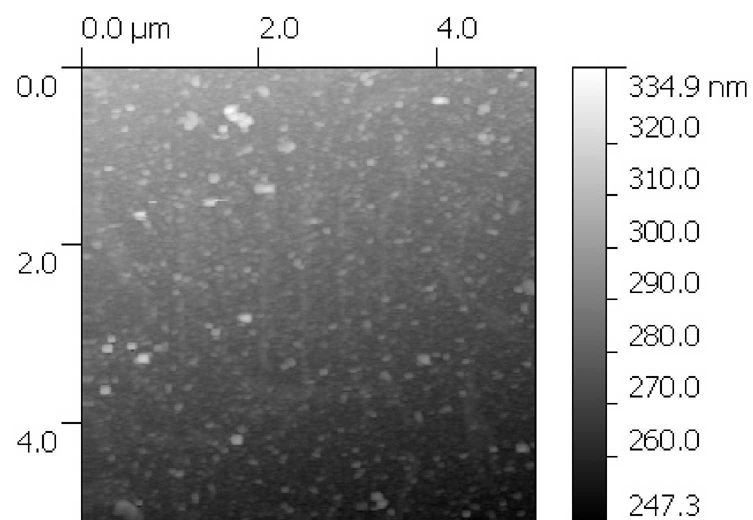

Figure 3.3 AFM image of sodium sulphate at set point 2.4V

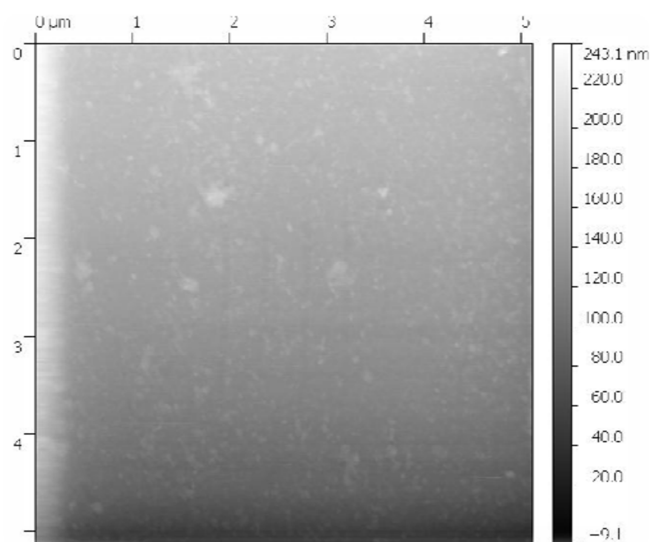

Figure 3.4 AFM image of sodium sulphate at set point 3.4V

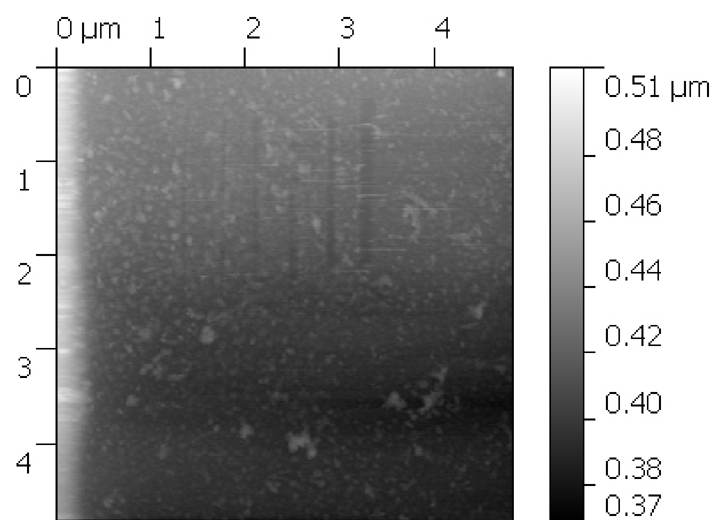

Figure 3.5 AFM image of sodium sulphate at set point 3.6V

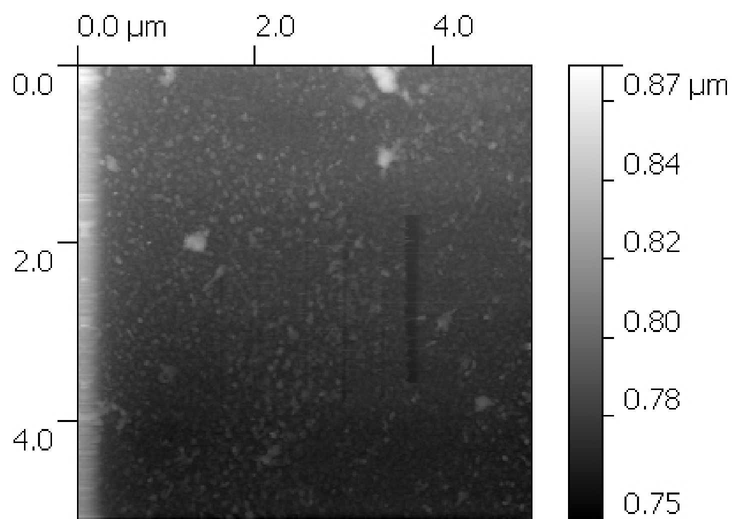

Figure 3.6 AFM image of sodium sulphate at set point of 3.8V

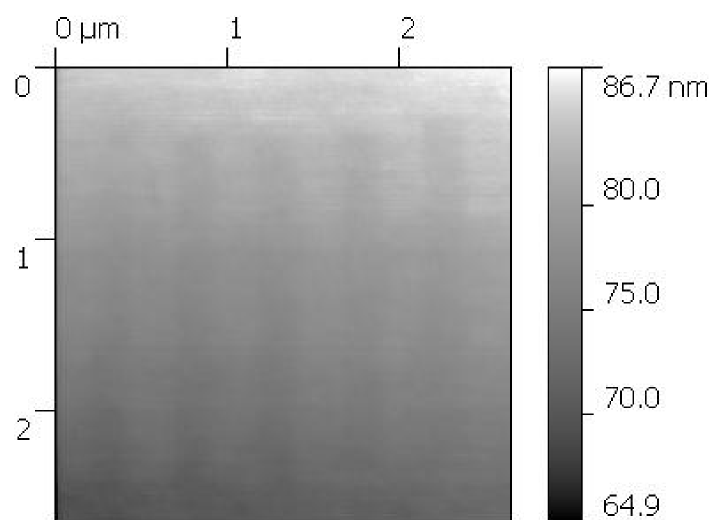

Figure 3.7 AFM image of sodium sulphate at set point of 4.8V

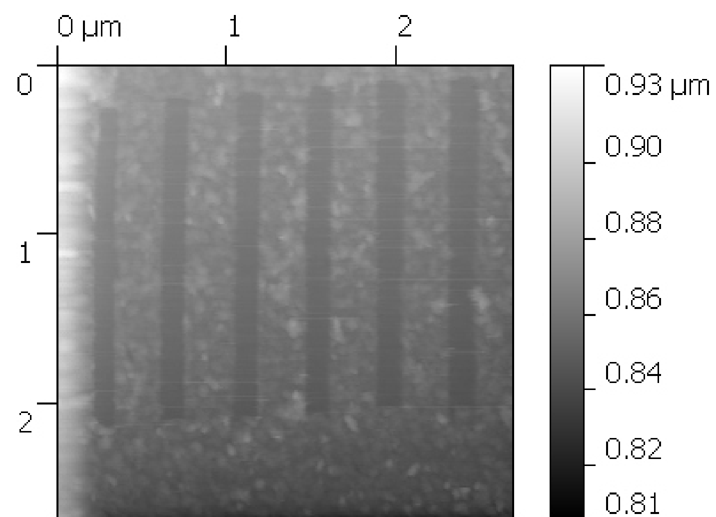

Figure 3.8 AFM image of sodium sulphate at set point of 5.8 V

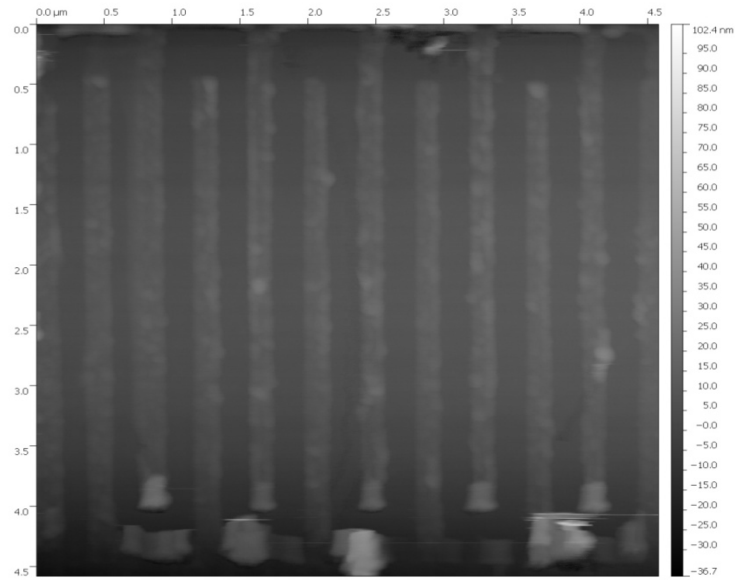

Figure 3.9 AFM image of sodium sulphate at set point of 6.8V

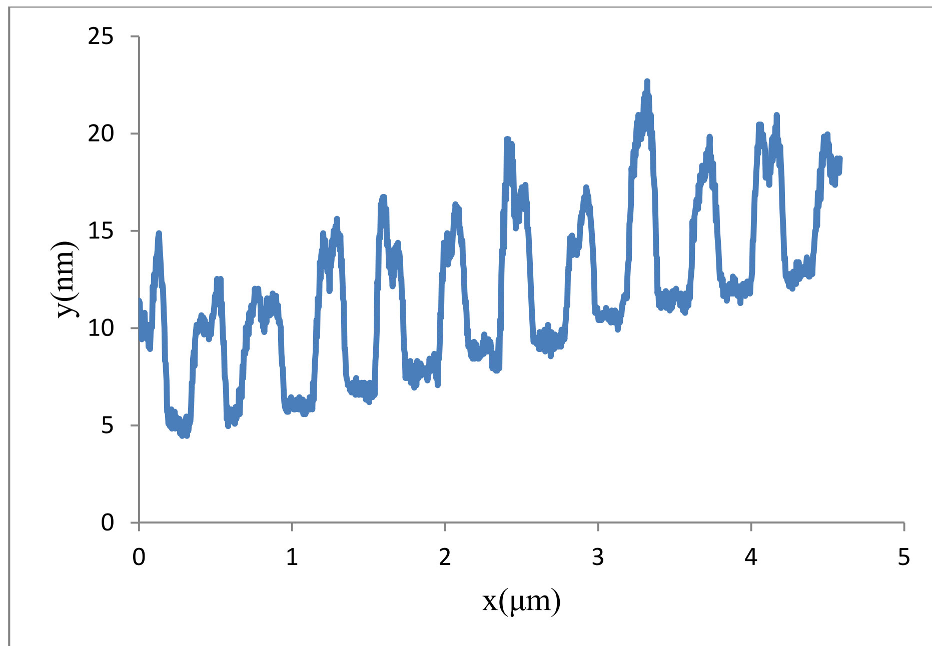

Figure 3.10 Profile line of patterned area in Figure 3.9V

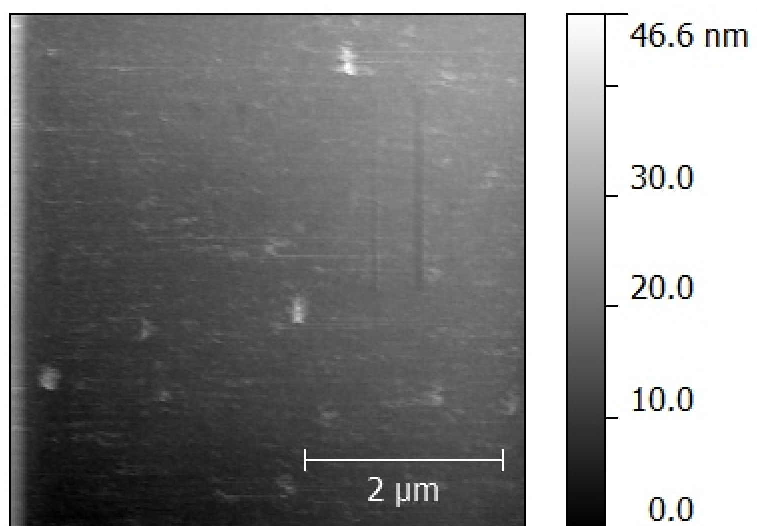

Figure 3.11 AFM image of potassium sulphate at set point 2.0V

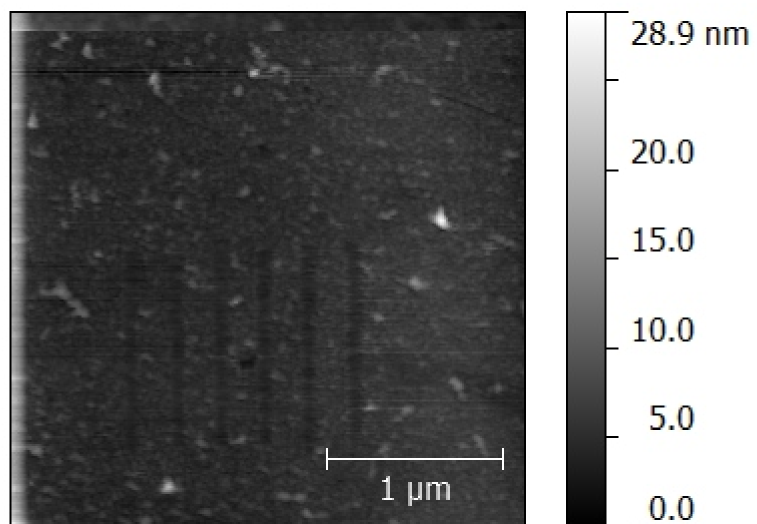

Figure 3.12 AFM image of potassium sulphate at set point of 3.0V

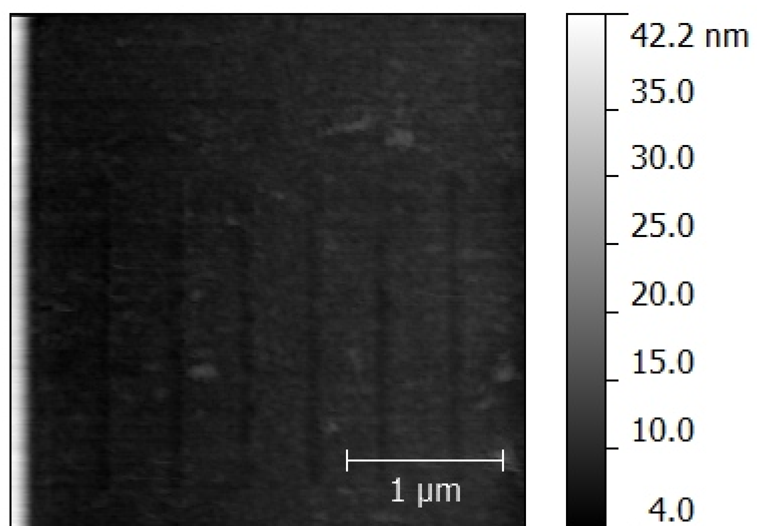

Figure 3.13 AFM image of potassium sulphate at set point of 4.0V

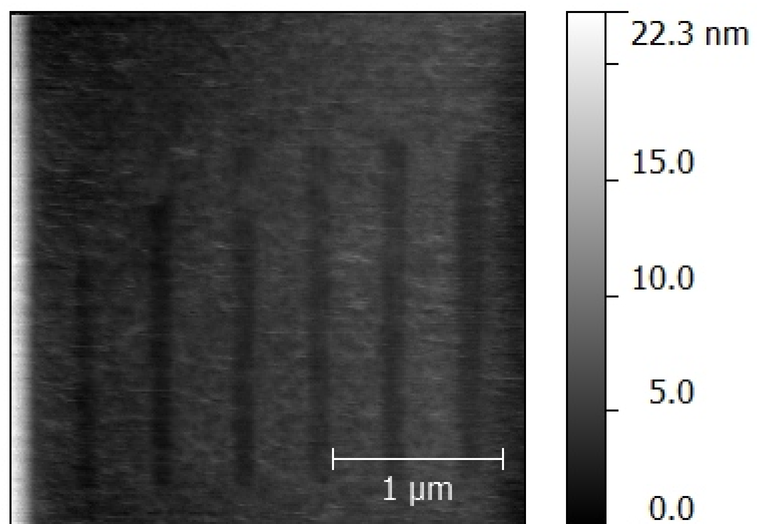

Figure 3.14 AFM image of potassium sulphate at set point of 5.0V

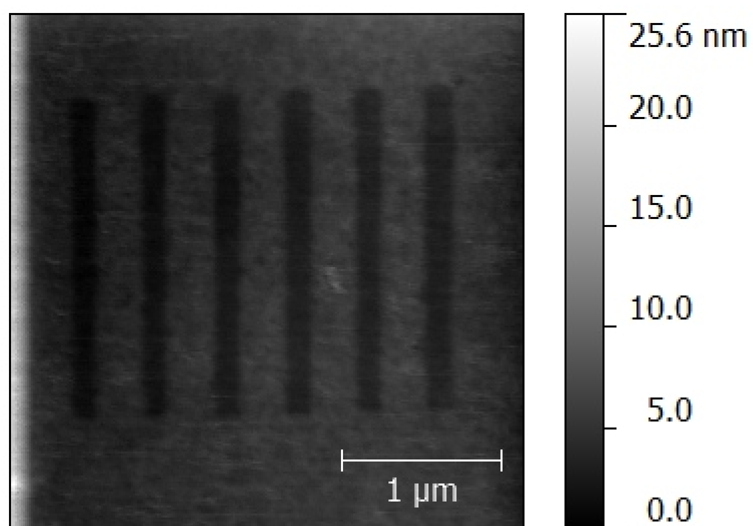

Figure 3.15: AFM image of potassium sulphate at set point of 6.0V

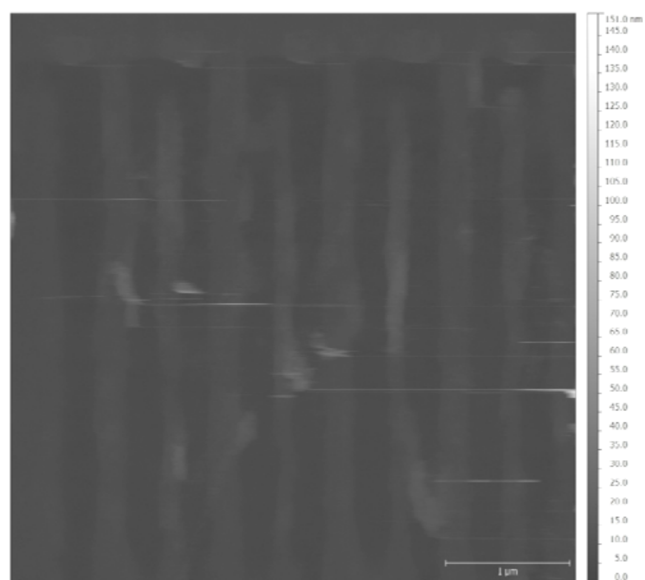

Figure 3.16 AFM image of potassium sulphate at set point 6.0V

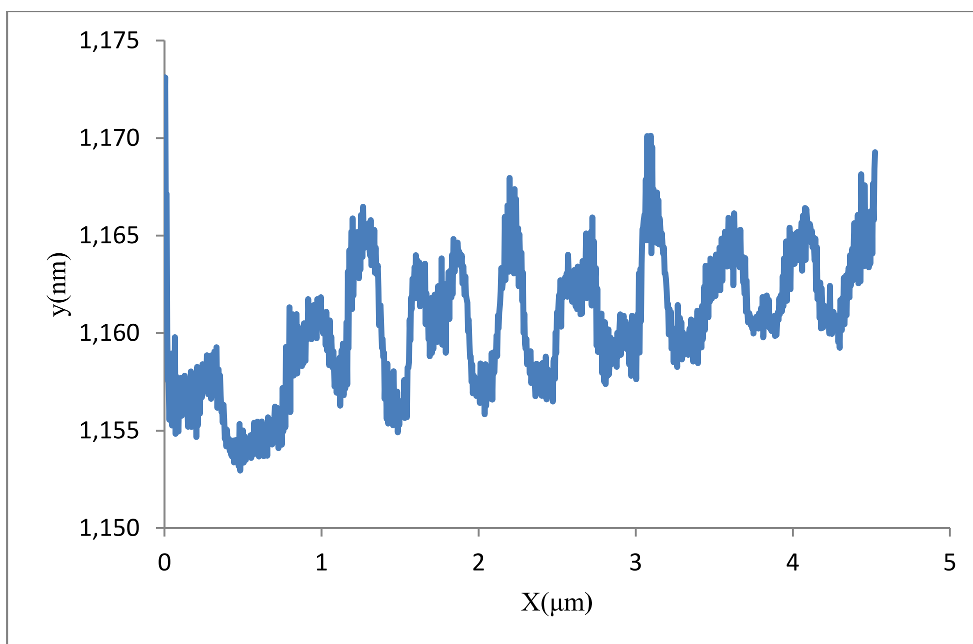

Figure 3.17 Profile line of the patterned area in Figure 3.16

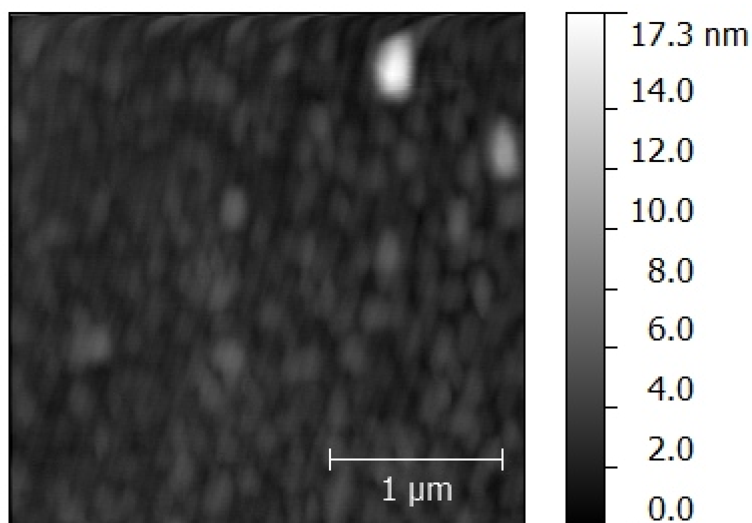

Figure 3.18 AFM image of the magnesium sulphate at set point of 2.0V

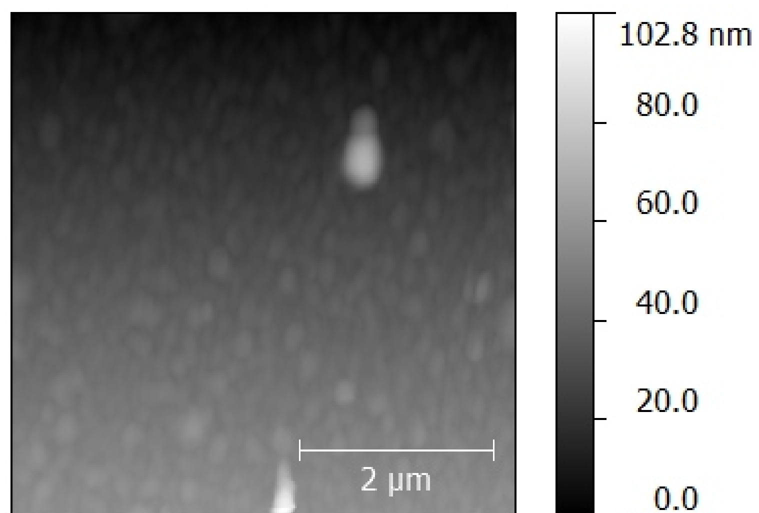

Figure 3.19 AFM image of the magnesium sulphate at set point of 3.0V

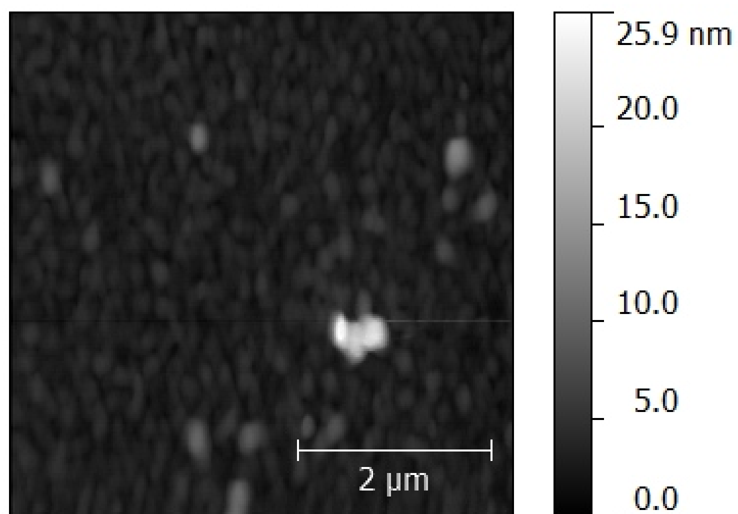

Figure 3.20 AFM image of the magnesium sulphate at set point of 4.0V

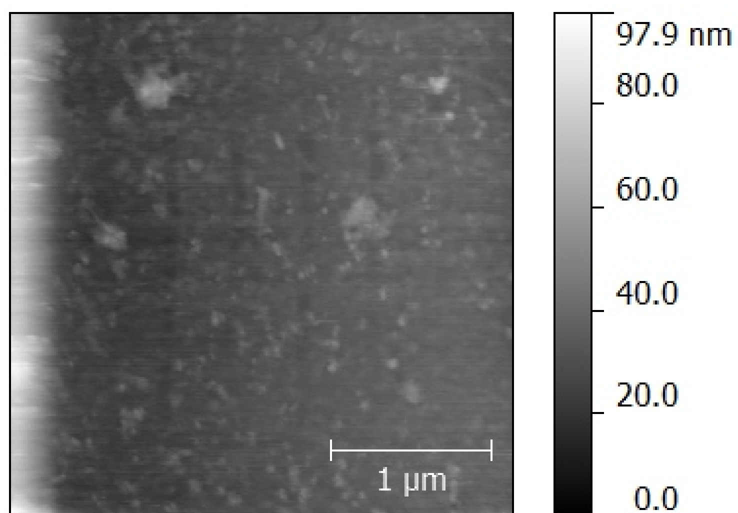

Figure 3.21 AFM image of the magnesium sulphate at set point of 5.0V

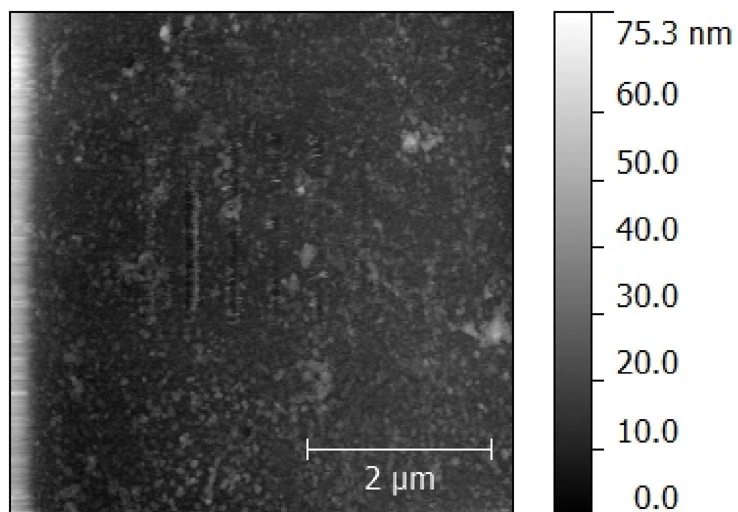

Figure 3.22 AFM image of the magnesium sulphate at set point 6.0V

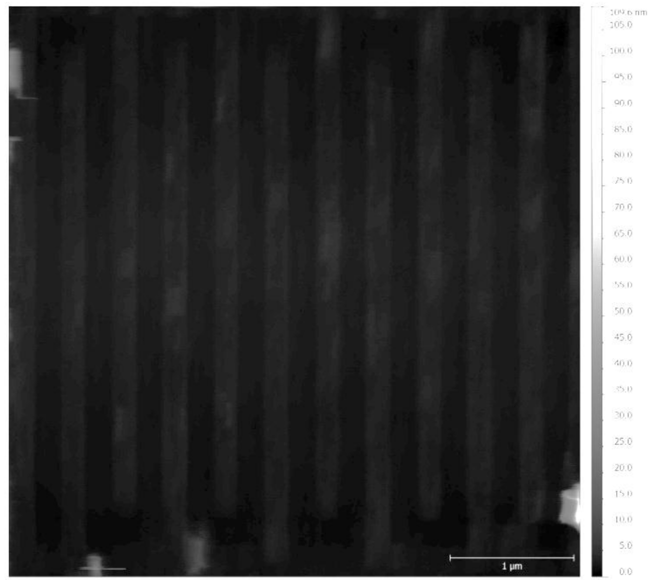

Figure 3.23 AFM image of the magnesium sulphate with the F tip at set point of 0.8V

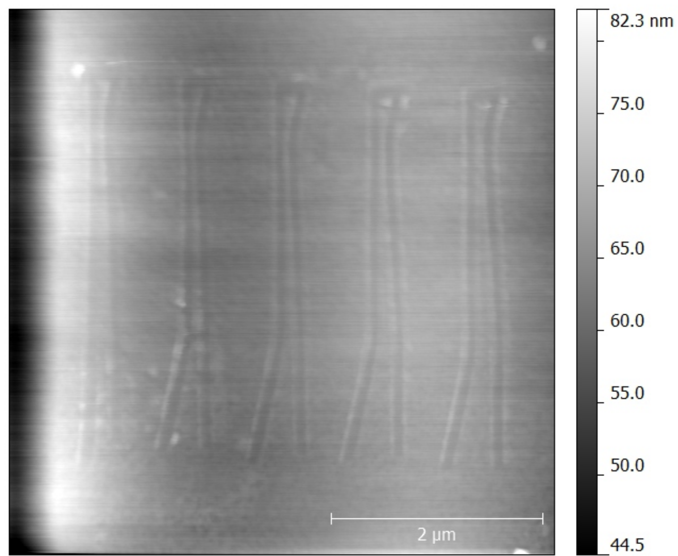

Figure 3.24 AFM image of magnesium sulphate with the F tip at set point of 4.5V

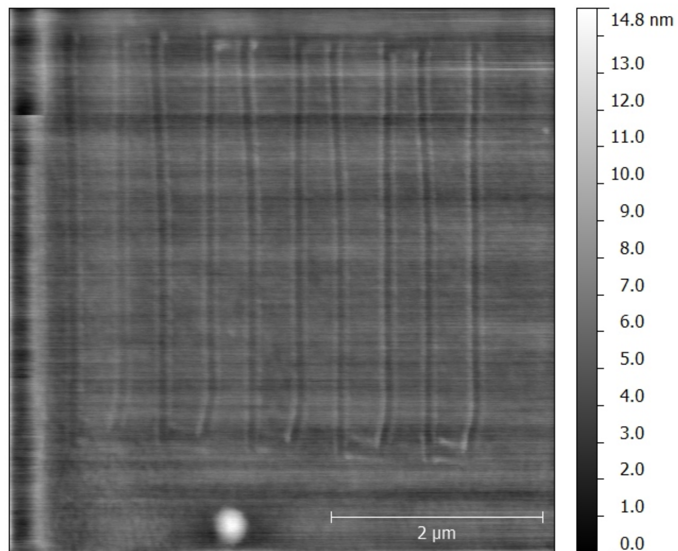

Figure 3.25 AFM image of magnesium sulphate with the F tip at set point of 5.4V

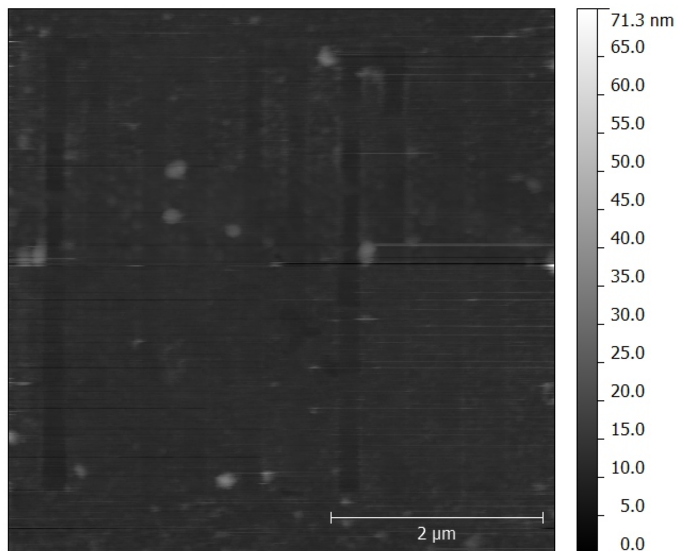

Figure 3.26 AFM image of magnesium sulphate with the F tip at set point of 6.3V

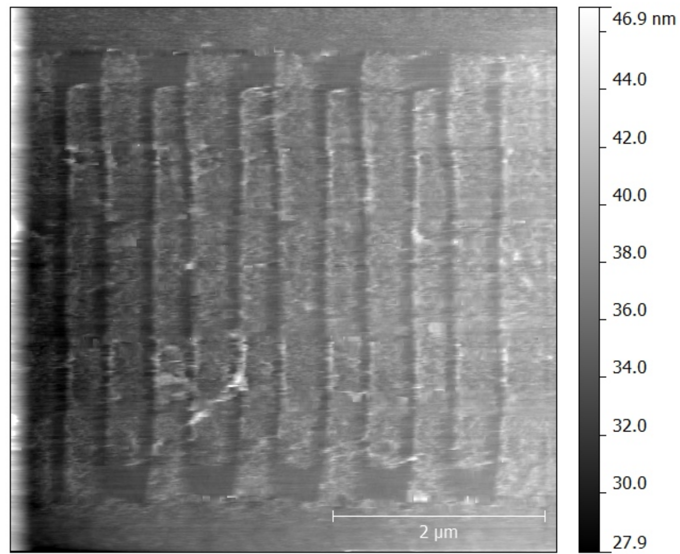

Figure 3.27 AFM image of magnesium sulphate with the F tip at set point of 7.0V

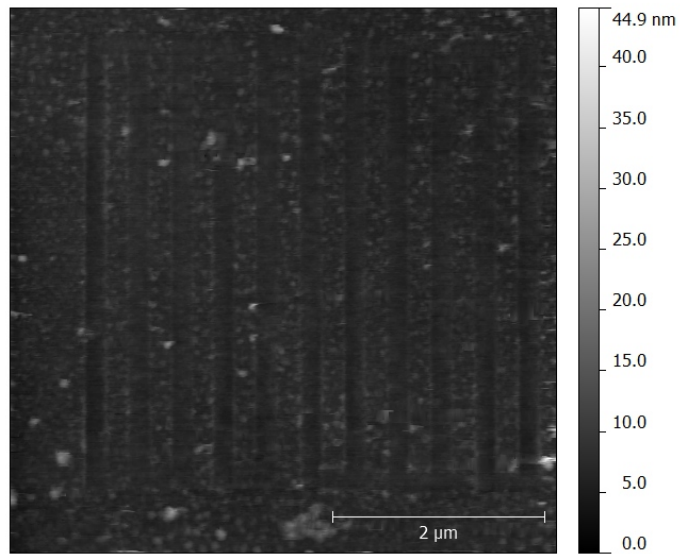

Figure 3.28 AFM image of magnesium sulphate with the F tip at set point of 7.2V

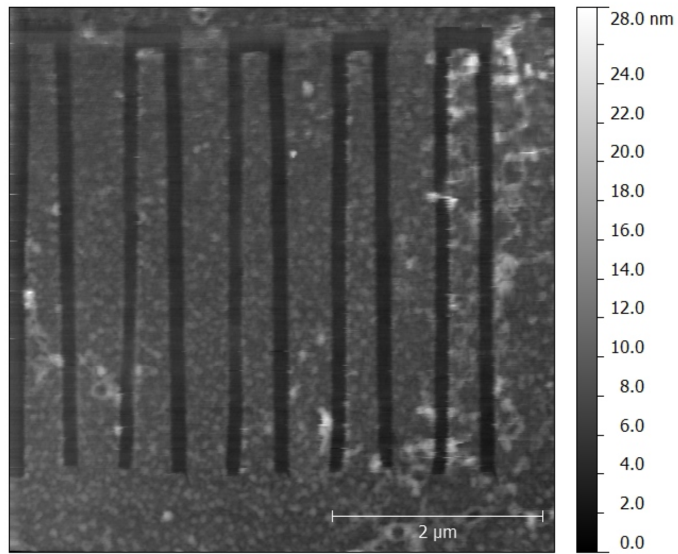

Figure 3.29 AFM image of magnesium sulphate with the F tip at set point of 7.9V

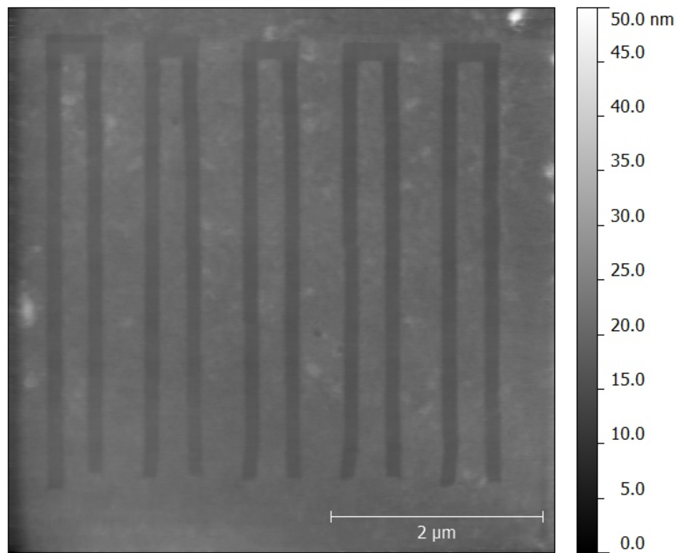

Figure 3.30 AFM image of Magnesium Sulphate with the F tip at set point of 8.9V

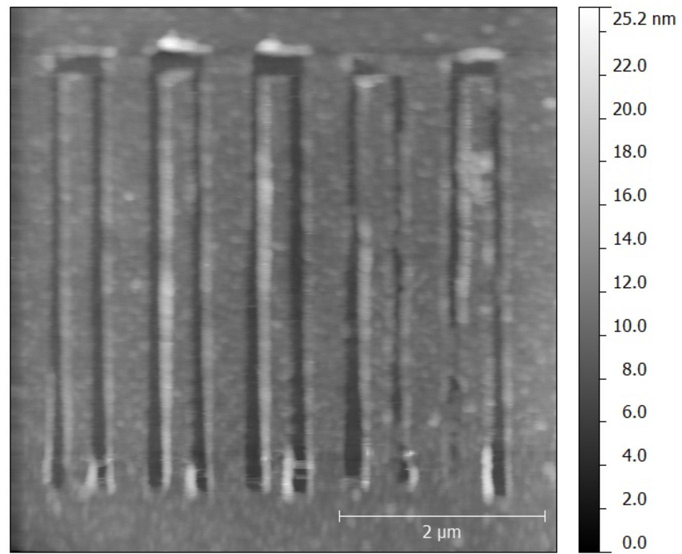

Figure 3.31 AFM image of Magnesium sulphate with the Multi -75 tip at set point of 2.0V

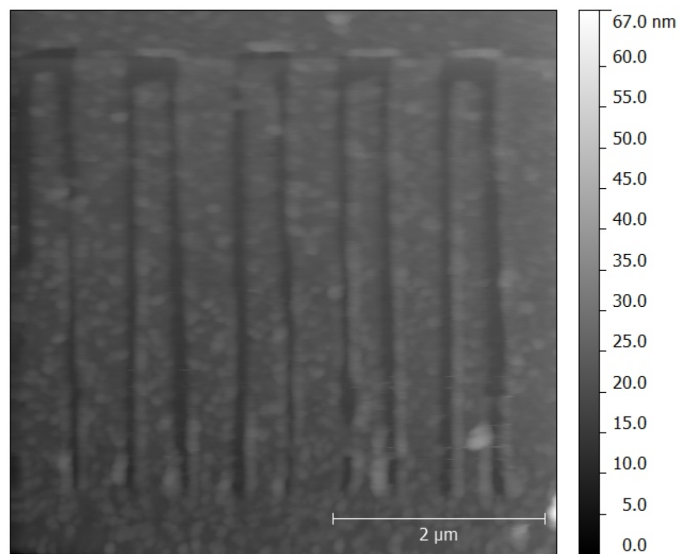

Figure 3.32 AFM image of the Magnesium Sulphate with the Multi 75 tip at set point of 3.0V

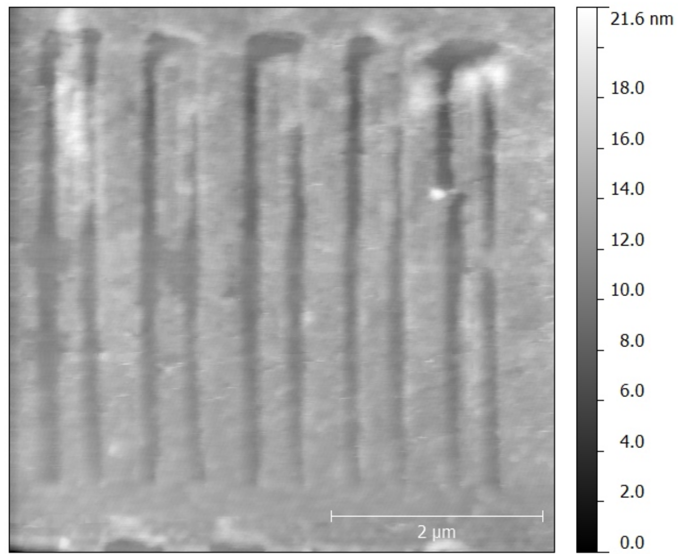

Figure 3.33 AFM image of the magnesium sulphate with Multi 75 tip at set point of 4.0V

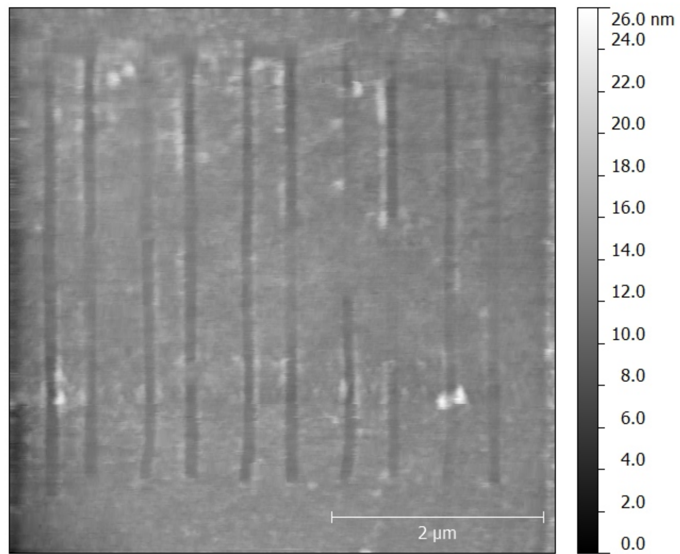

Figure 3.34 AFM image of magnesium sulphate with Multi 75 tip at set point of 5.0V

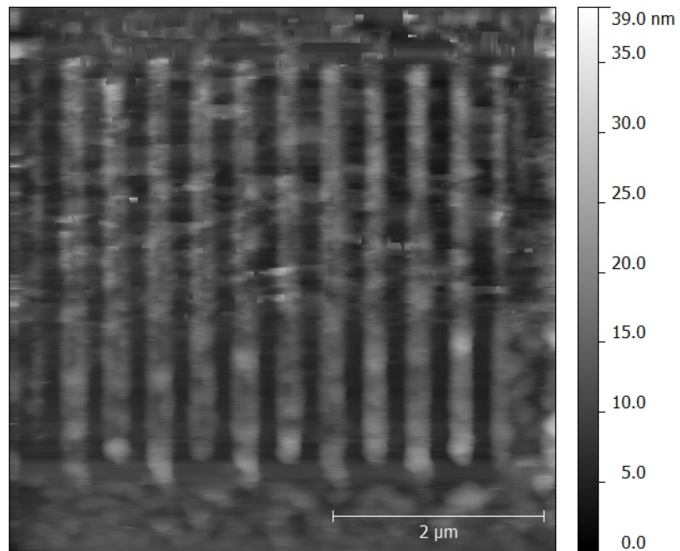

Figure 3.35 AFM image of Magnesium Sulphate with Multi 75 tip at set point of 5.9V

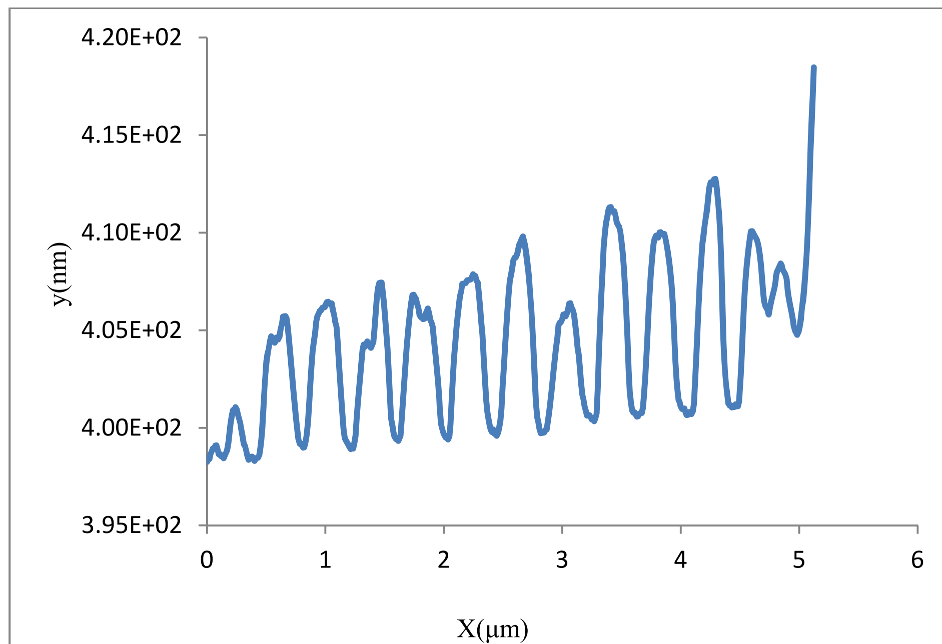

Figure 3.36 profile line of the patterned area in Figure 3.34

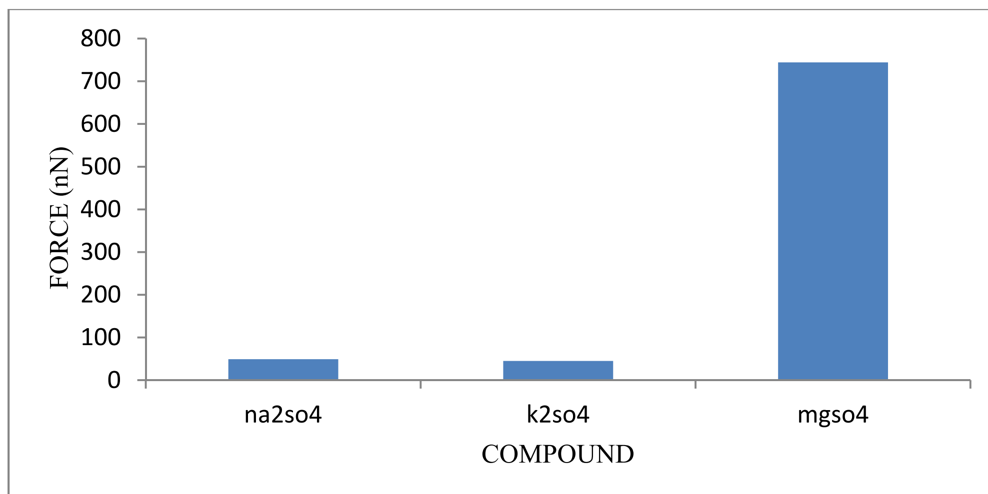

Figure 3.37 spreadsheet showing the relation between the compound and the force

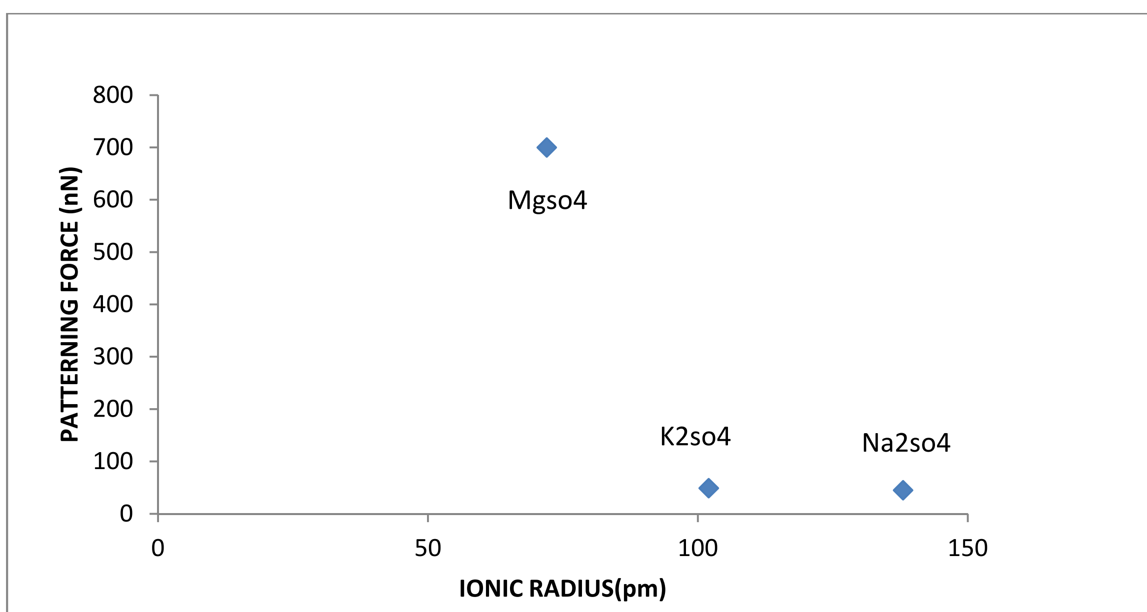

Figure3.38 Spreadsheet showing a relation between the compound force constant and ionic radius.

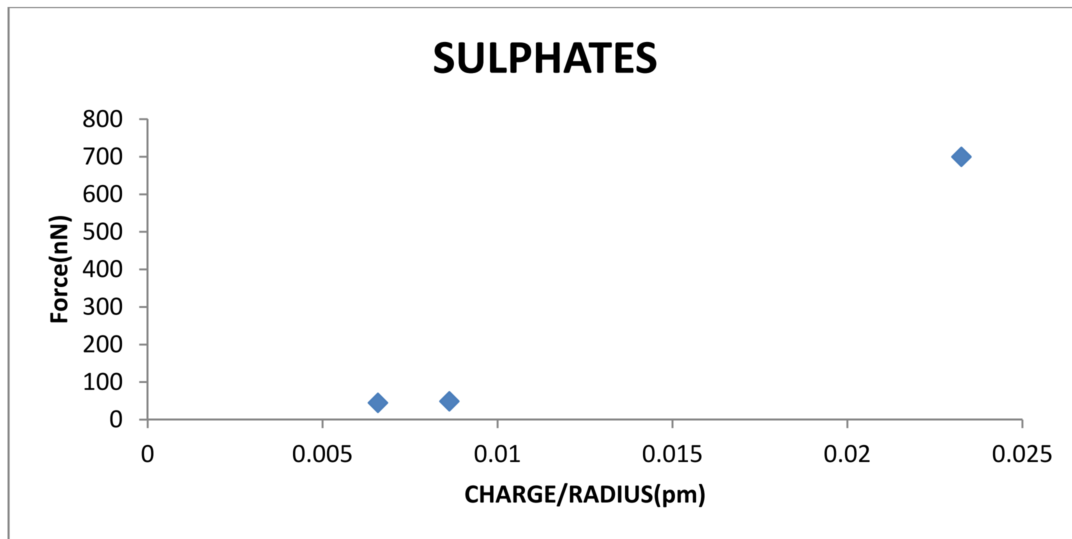

Figure 3.39 Spreadsheet showing a relation between the force and charge of ion/ionic radius

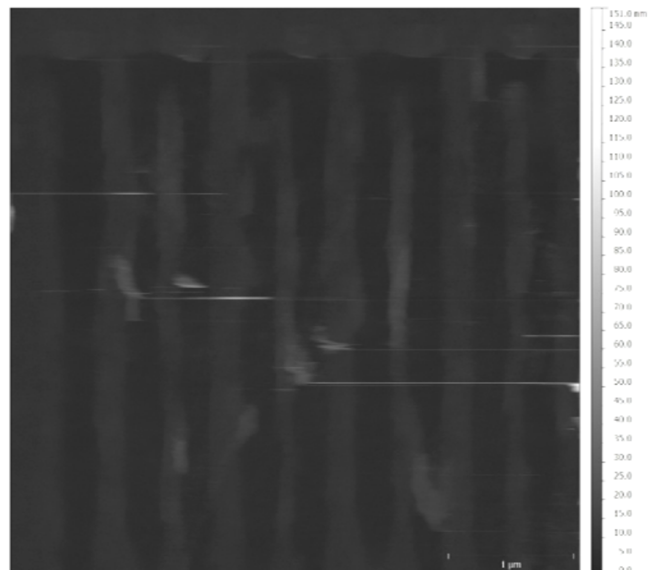

Figure 3.40 AFM image of sodium fluoride at set point of 1.0V

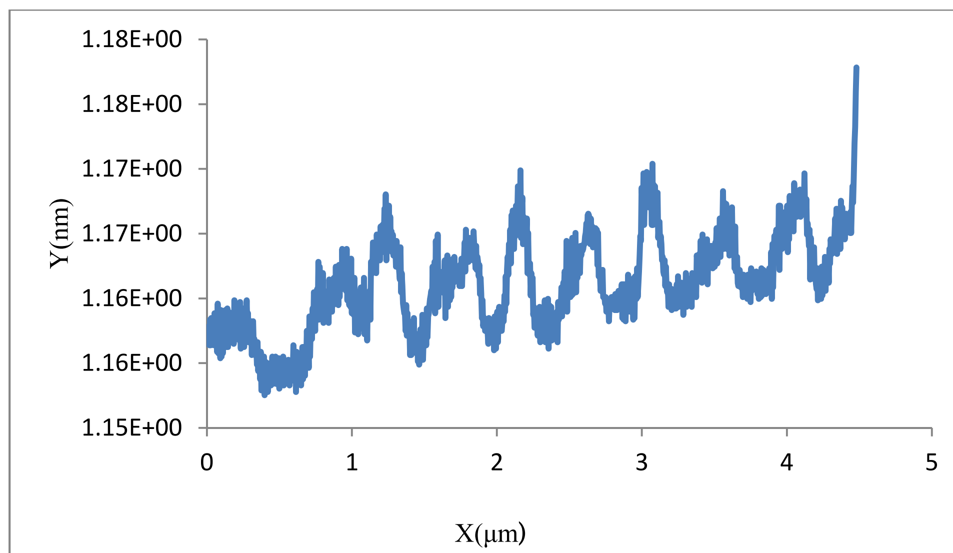

Figure 3.41 Profile line of patterned area in Figure 3.22

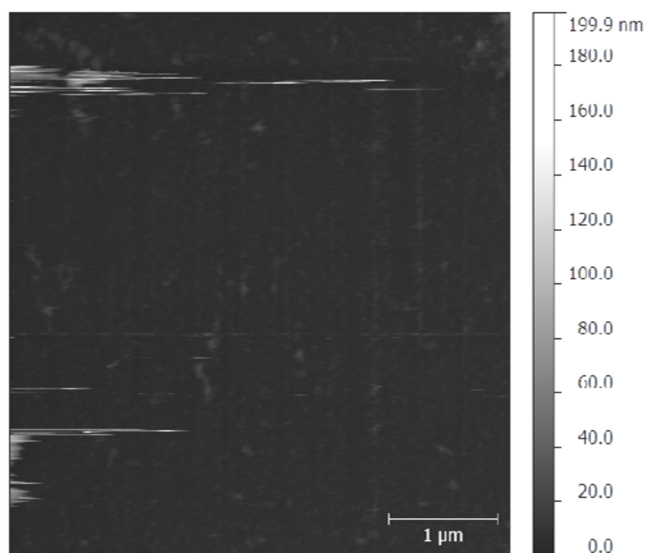

Figure 3.42 AFM image of the sodium chloride at set point of 0.8V

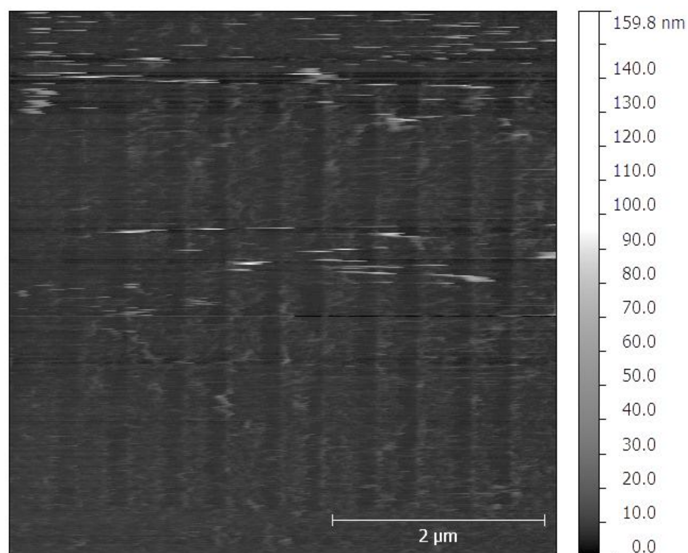

Figure 3.43 AFM image of the sodium chloride at set point of 1.0V

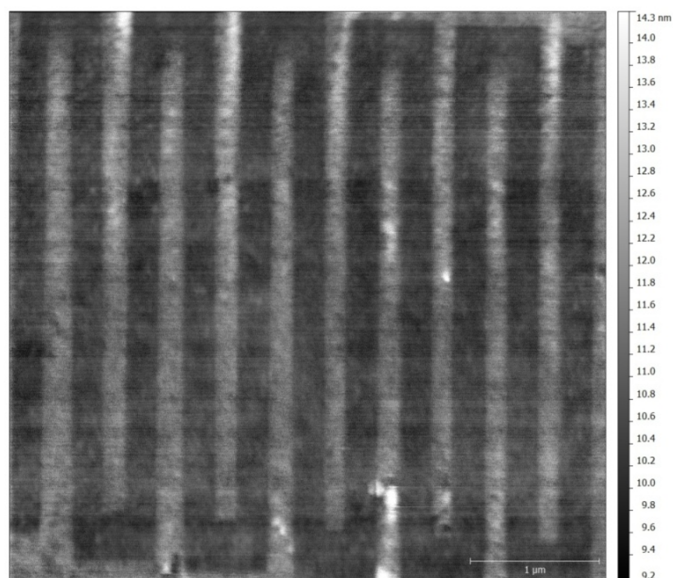

Figure 3.44 AFM image of the sodium chloride at set point of 1.9V

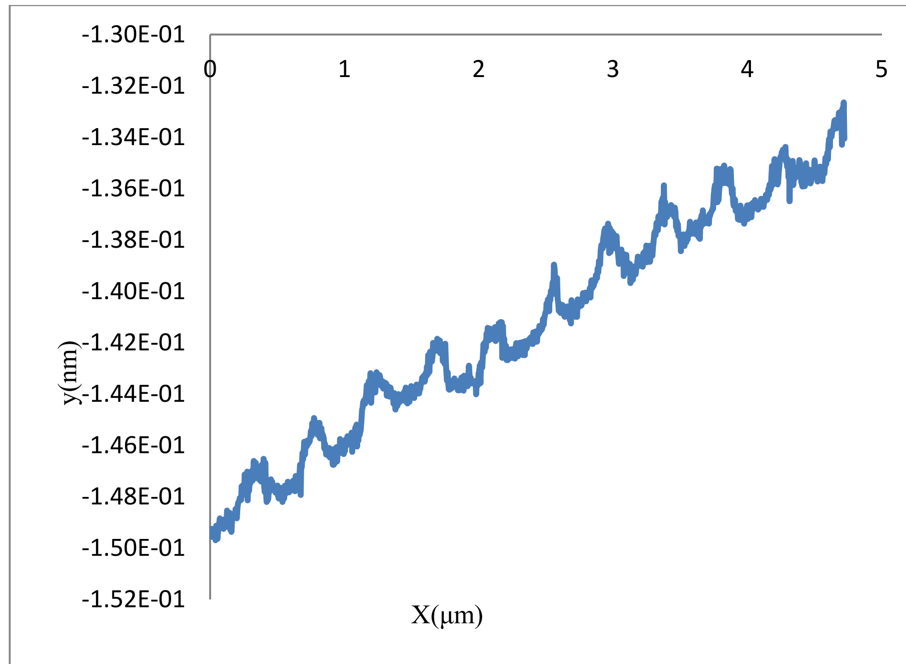

Figure 3.45 Profile line of the patterned area in Figure 3.26V

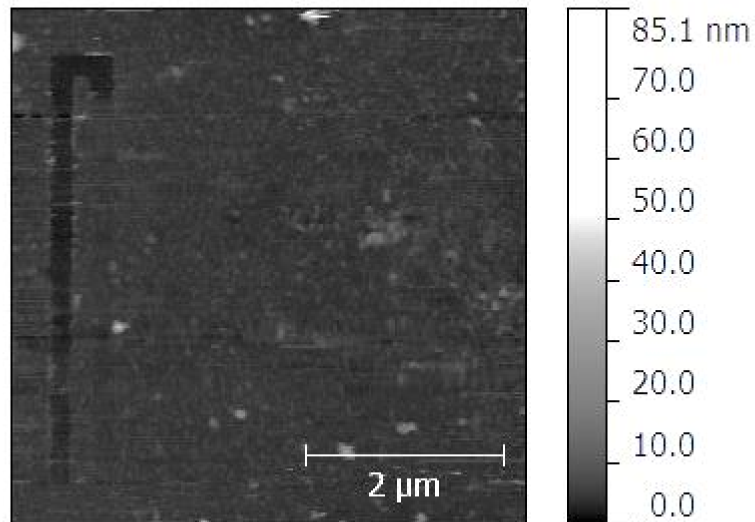

Figure 3.46 AFM image of Sodium bromide at set point of -0.3V

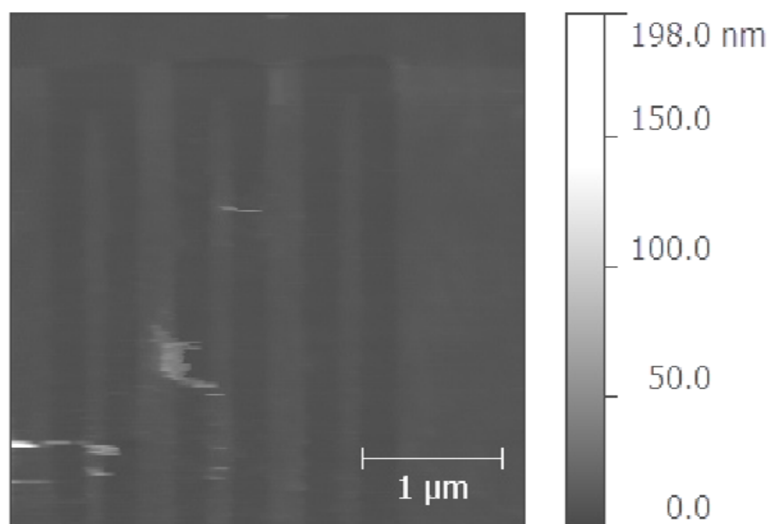

Figure 3.47 AFM image of Sodium bromide at set point of 1.0V

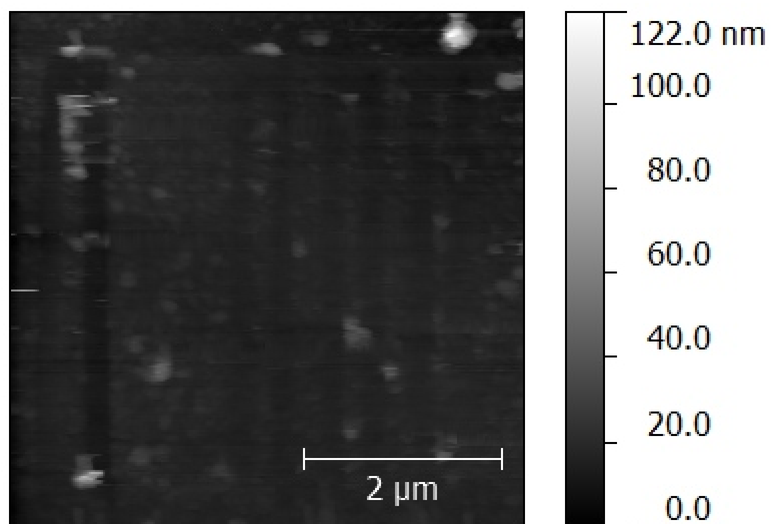

Figure 3.48 AFM image of Sodium bromide at set point of 2.2V

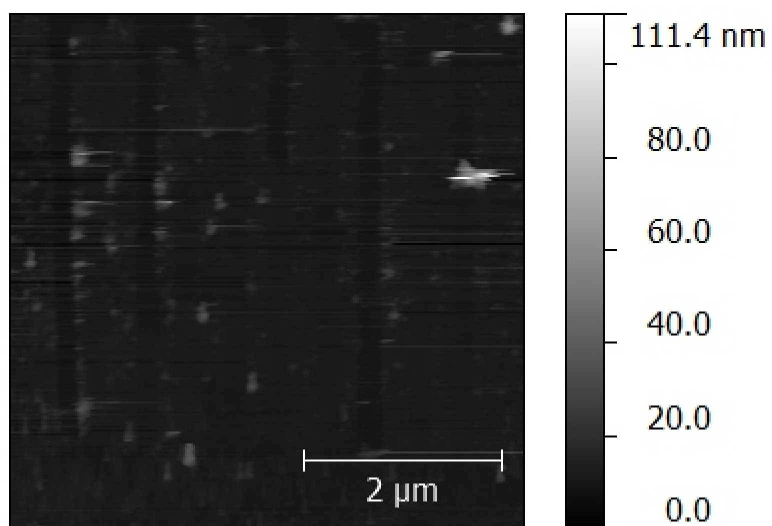

Figure 3.49 AFM image of Sodium bromide at set point of 3.7V

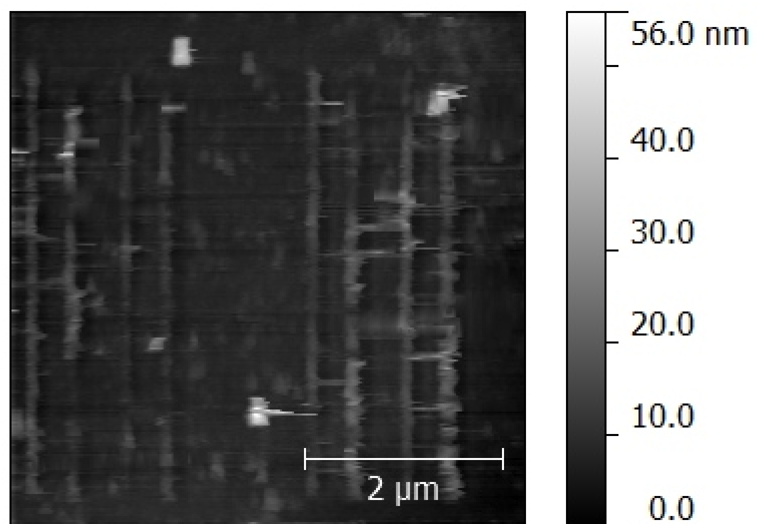

Figure 3.50 AFM image of Sodium bromide at set point of 4.7V

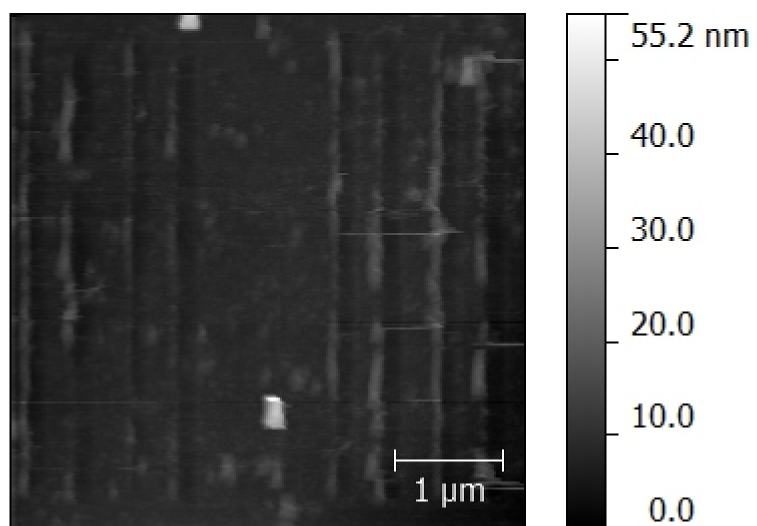

Figure 3.51 AFM image of Sodium bromide at set point of 5.2V

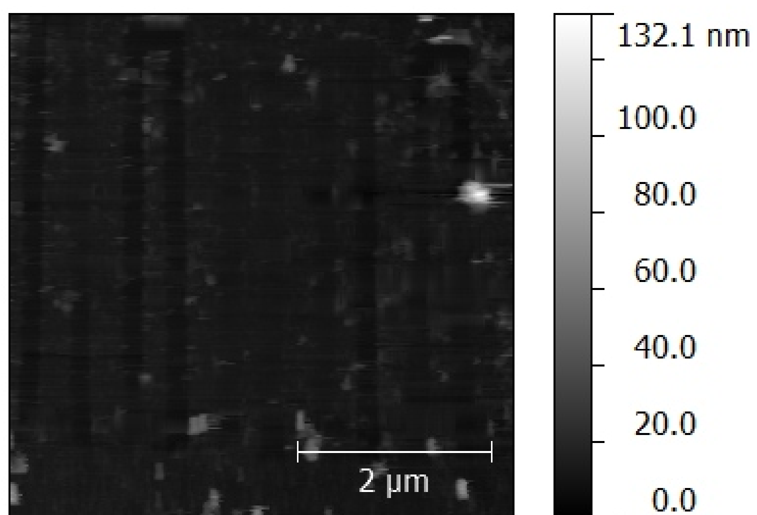

Figure 3.52 AFM image of Sodium bromide at set point of 6.2V

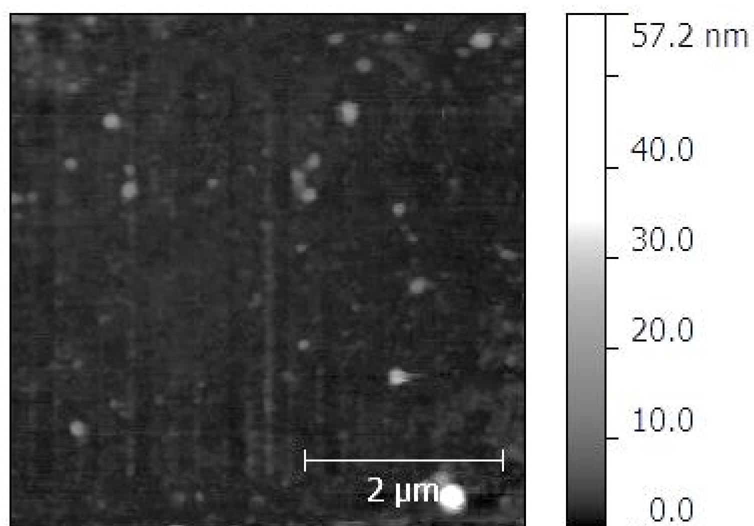

Figure 3.53 AFM image of Sodium bromide on F tip at set point of 0.1V

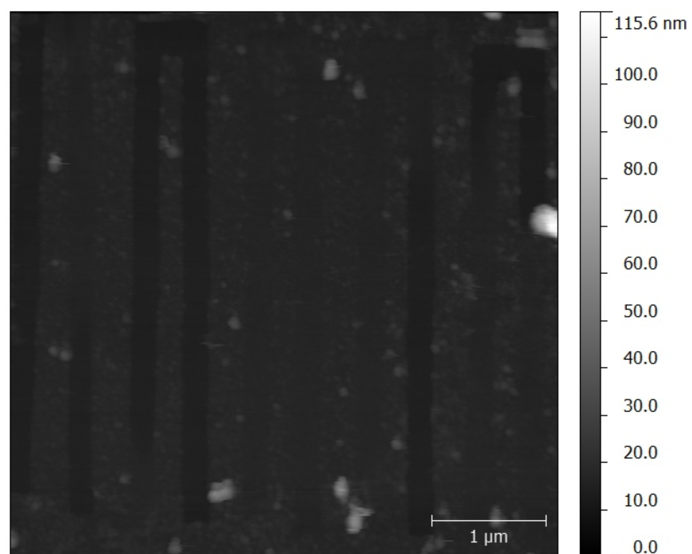

Figure 3.54 AFM image of Sodium bromide on F tip at set point of 3.2V

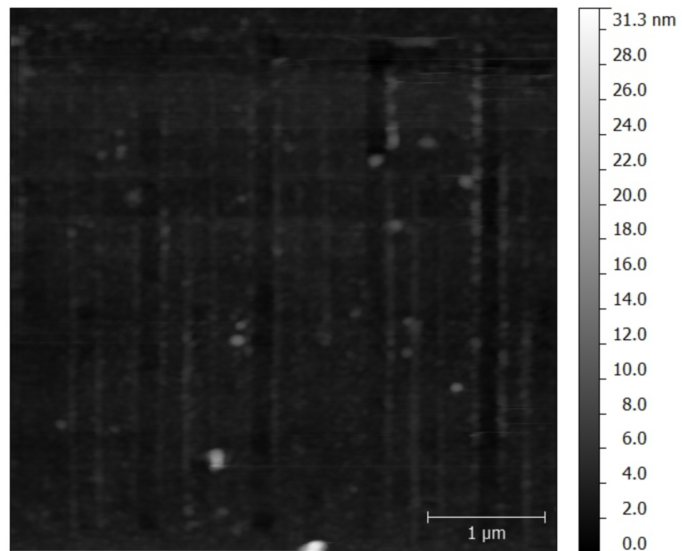

Figure 3.55 AFM image of Sodium bromide on F tip at set point of 5.2V

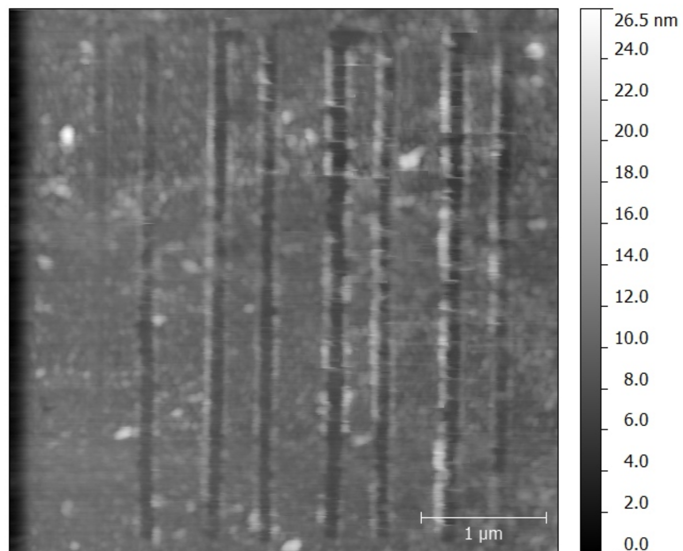

Figure 3.56 AFM image of Sodium bromide on F tip at set point of 5.4V

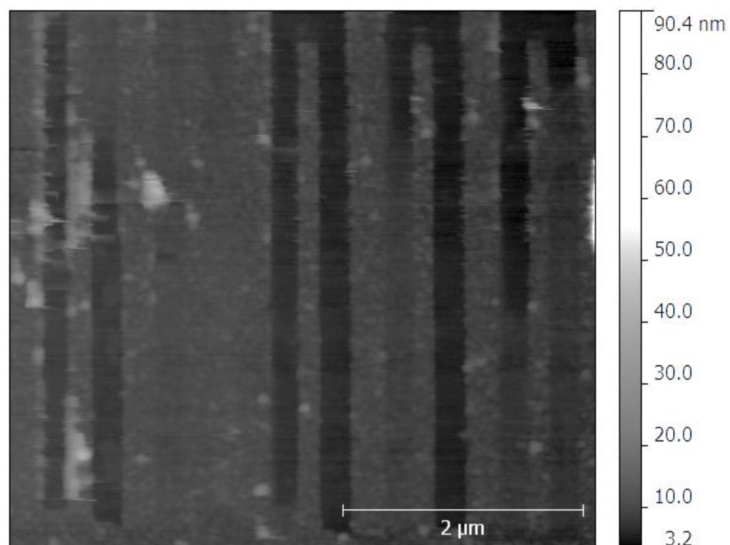

Figure 3.57 AFM image of Sodium bromide on F tip at set point of 5.8V

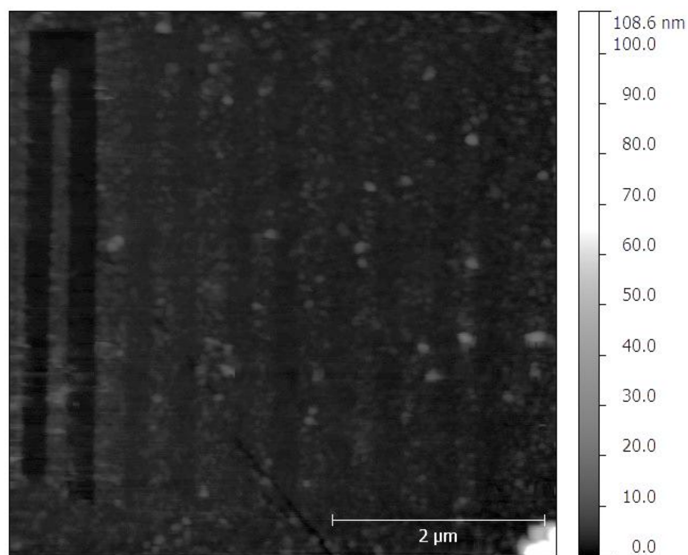

Figure 3.58 AFM image of Sodium bromide on F tip at set point of 7.0V

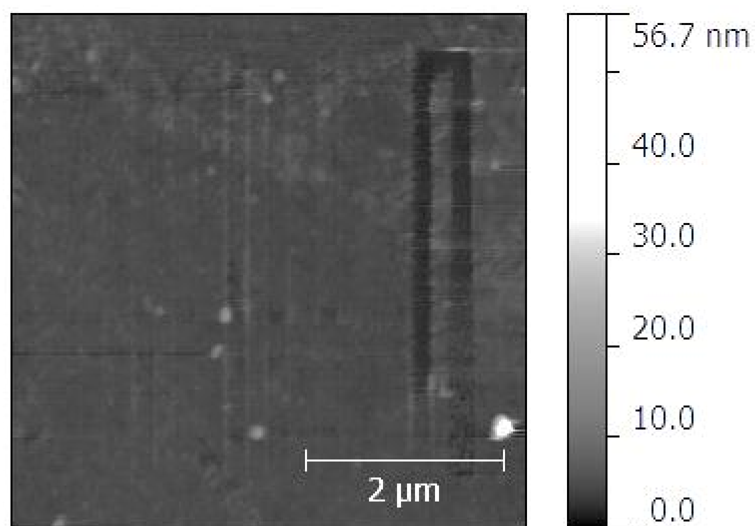

Figure 3.59 AFM image of the Sodium bromide on Multi -75 tip at set point of -0.3V

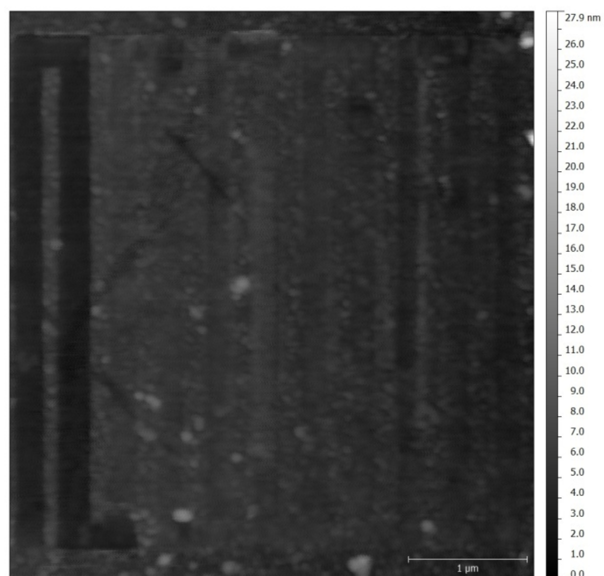

Figure 3.60 AFM image of the Sodium bromide on Multi -75 tip at set point of 2.9V

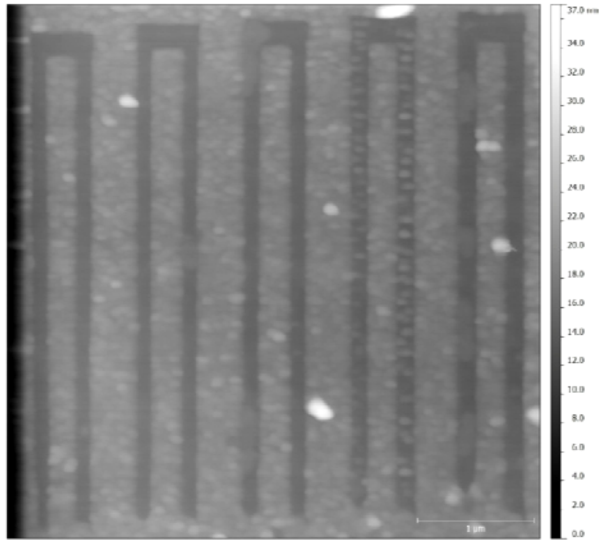

Figure 3.61 AFM image of Sodium bromide on Multi -75 tip at set point of 3.8V

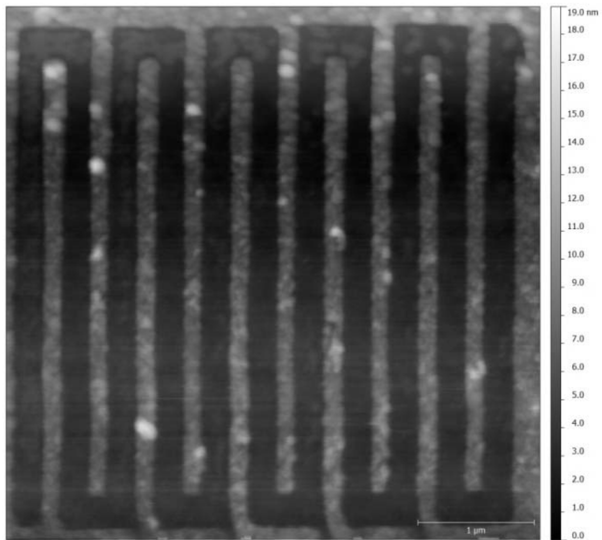

Figure 3.62 AFM image of the Sodium bromide on Multi-75 tip at set point of 5.9V

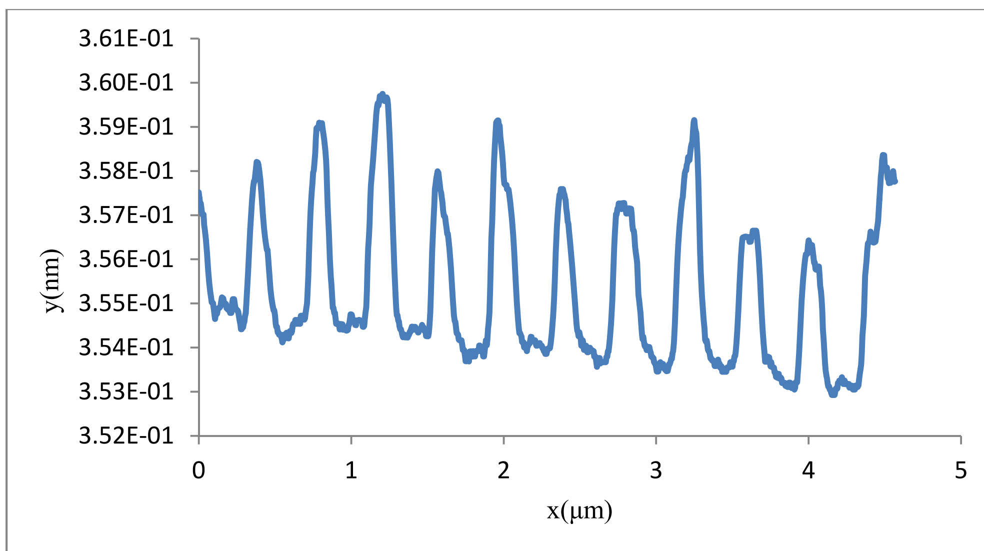

Figure 3.63: Profile line of the patterned area in Figure 3.44

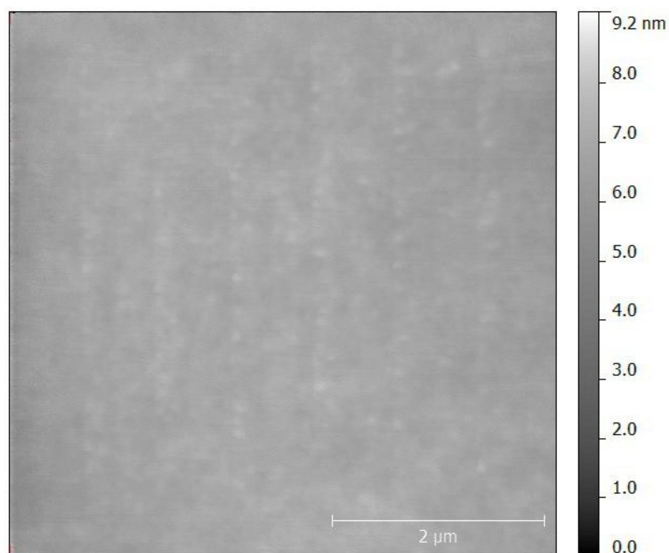

Figure 3.64: AFM image of Sodium iodide at set point of 3.0V

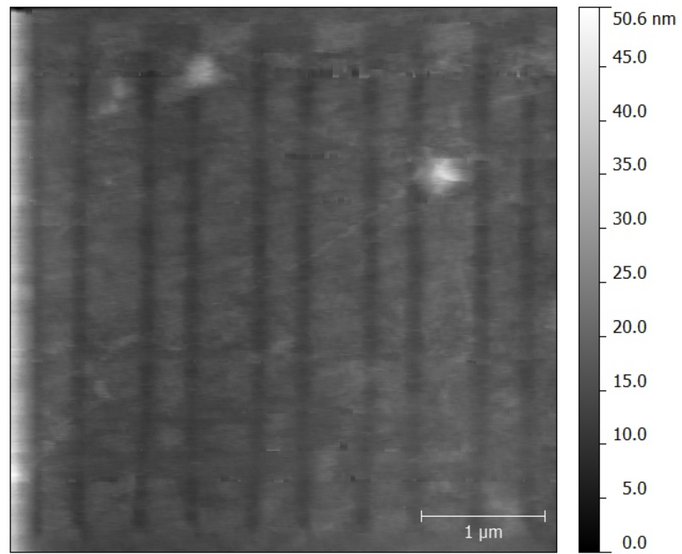

Figure 3.65: AFM image of the Sodium iodide at set point 3.1V

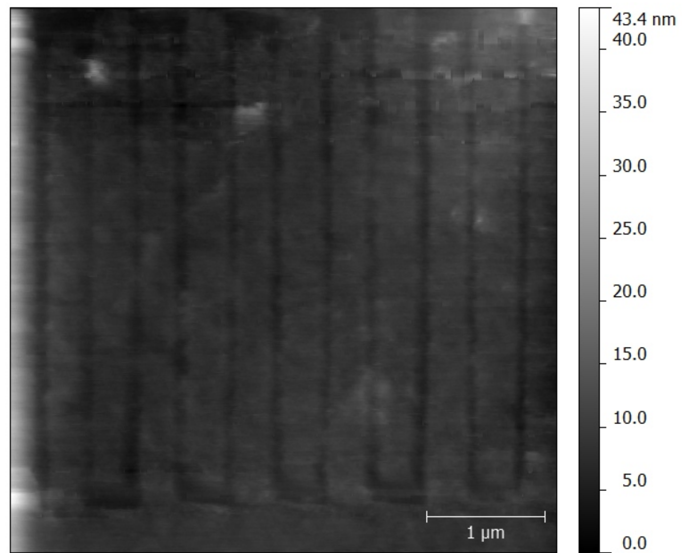

Figure 3.66 AFM image of Sodium iodide at set point of 3.6V

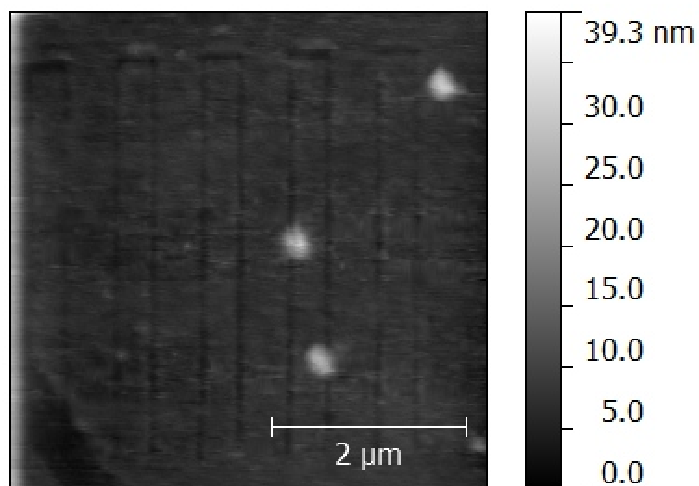

Figure 3.67: AFM image of Sodium iodide at set point of 4.2V

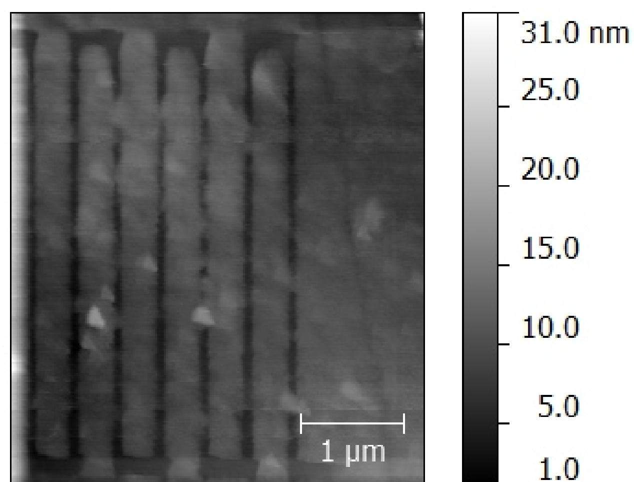

Figure 3.68: AFM image of Sodium iodide at set point of 4.5V

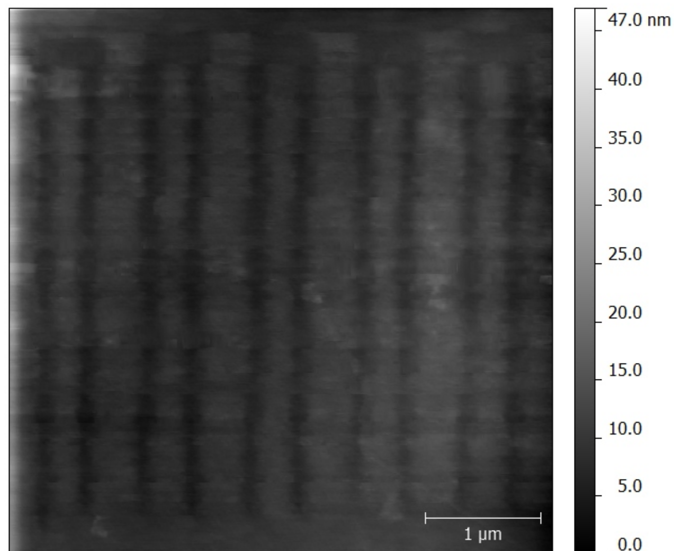

Figure 3.69 AFM image of Sodium iodide at set point of 4.8V

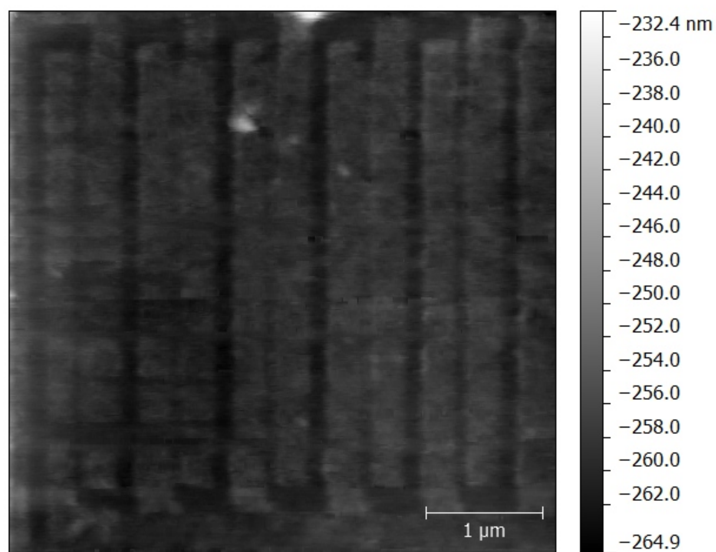

Figure 3.70 AFM image of sodium iodide at set point of 5.3V

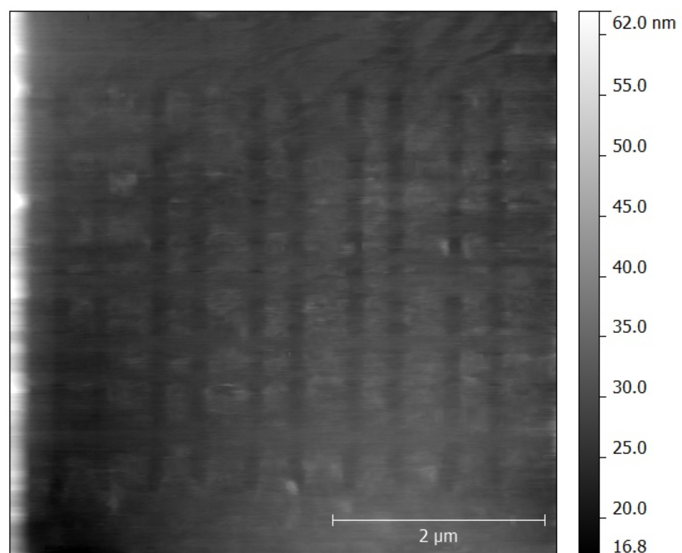

Figure 3.71 AFM image of Sodium iodide at set point of 5.7V

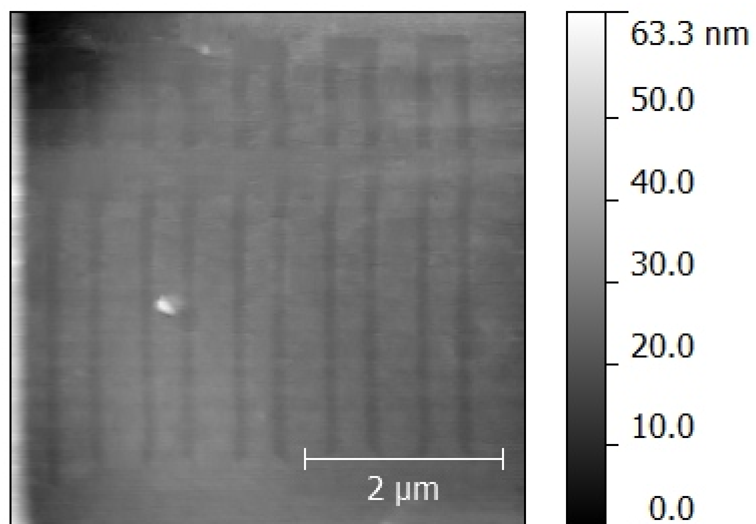

Figure 3.72: AFM image of Sodium iodide at set point of 6.3V

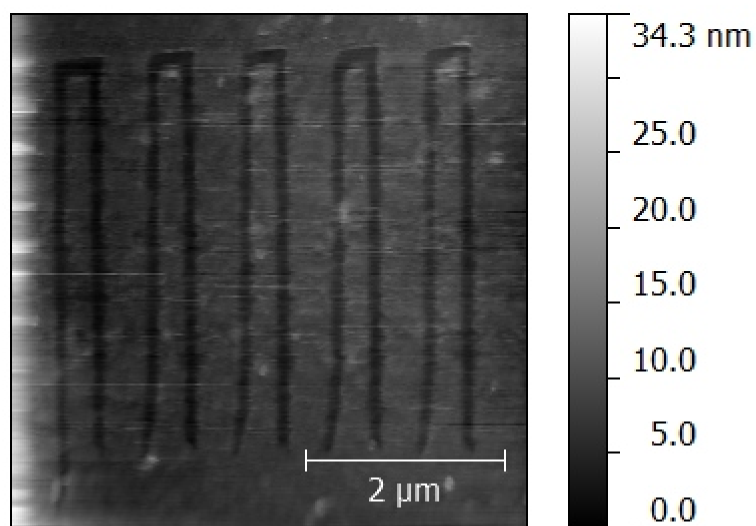

Figure 3.73 AFM image of Sodium iodide at set point of 7V

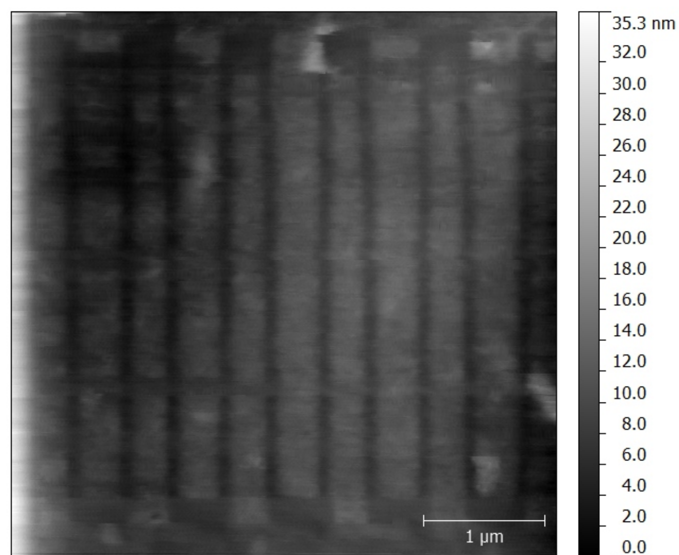

Figure 3.74: AFM image of the Sodium iodide at set point of 8.5V

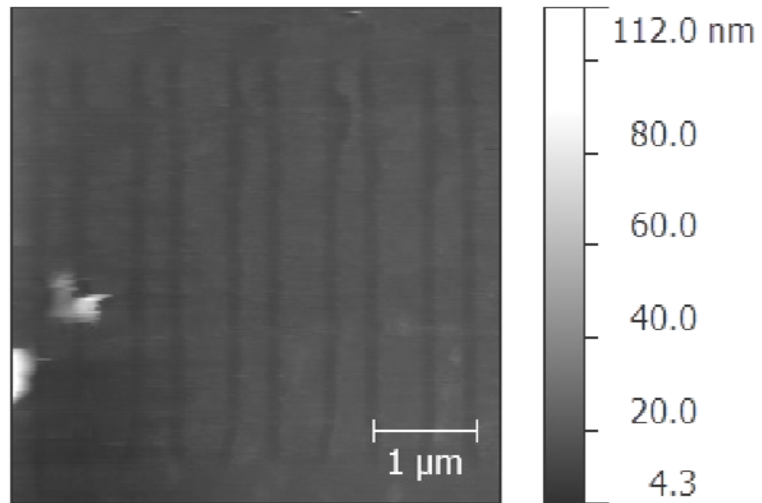

Figure 3.75: AFM image of the Sodium iodide at set point of 9V

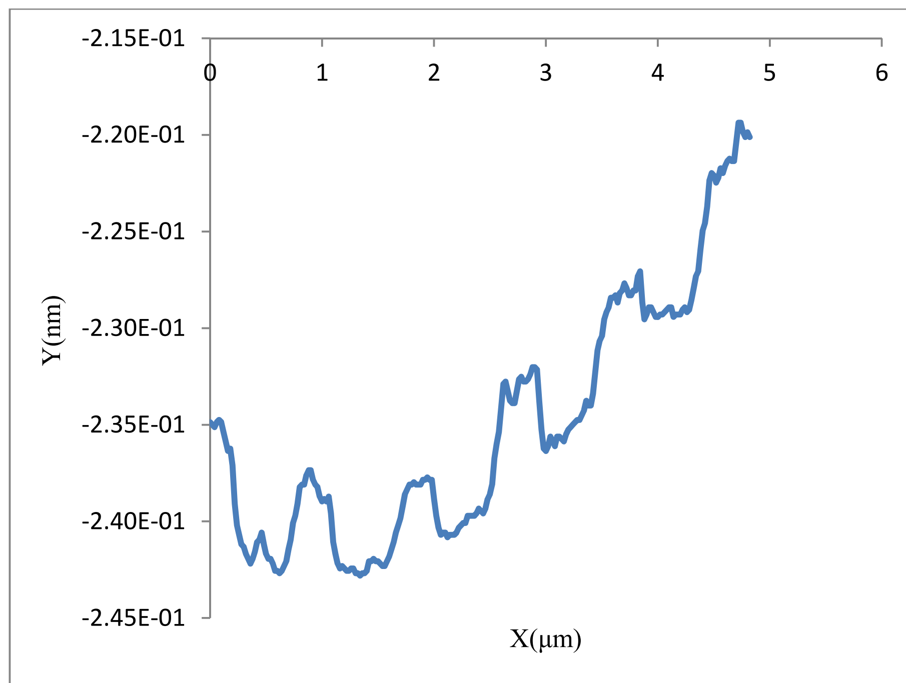

Figure 3.76: Profile line of the patterned area in Figure 3.58

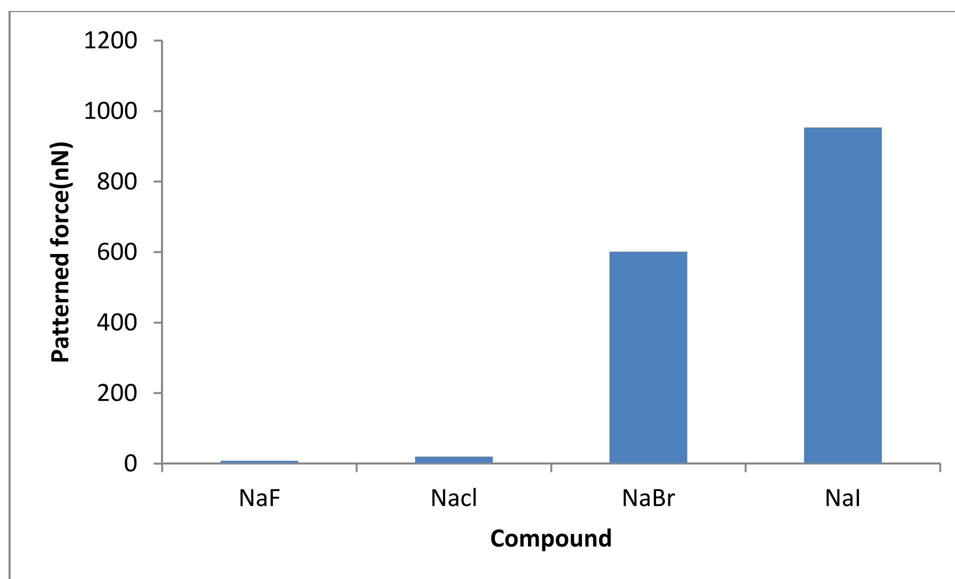

Figure 3.77: Spreadsheet showing the relation between the force taken to get patterned by the compound.

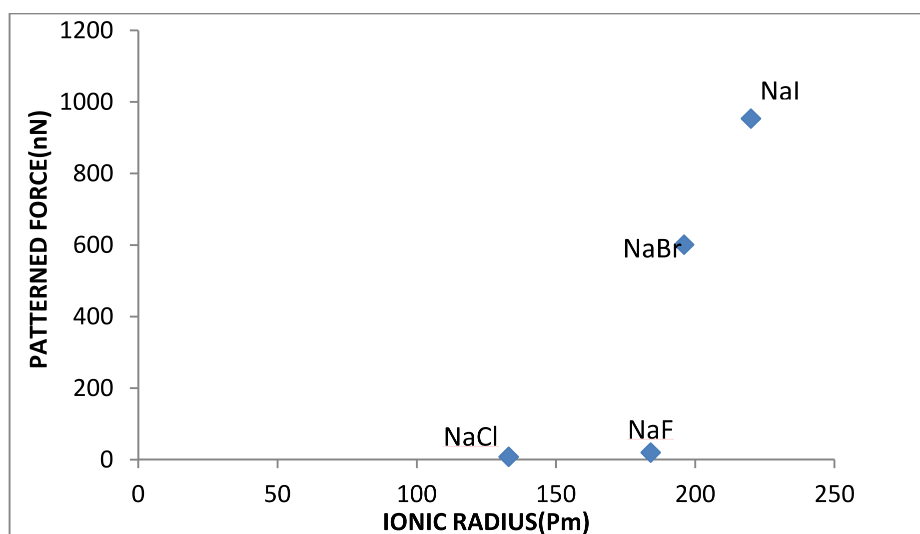

Figure 3.78: Spreadsheet showing the relation between the force constant and ionic radius of the compound.

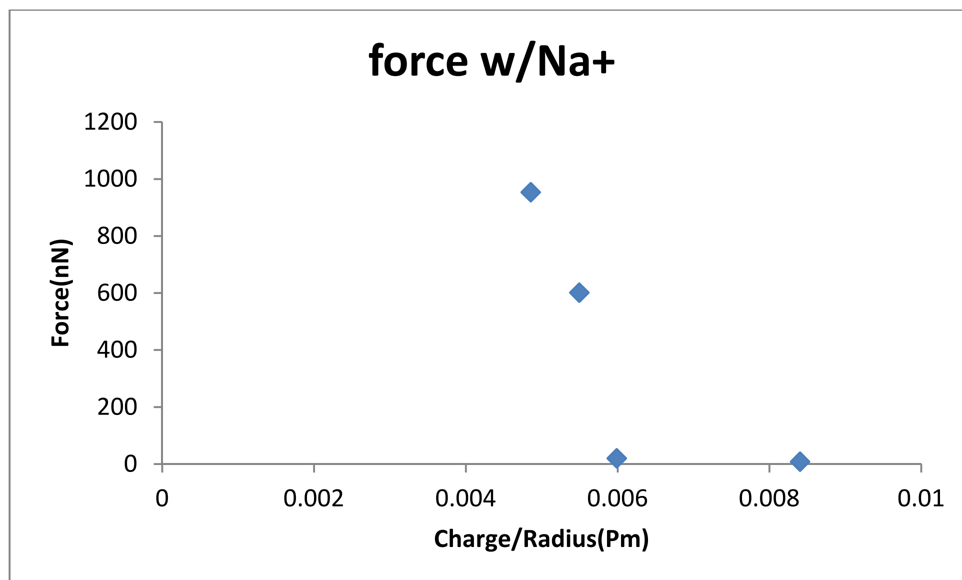

Figure 3.79: Spreadsheet showing the relation between the force and charge/Radius

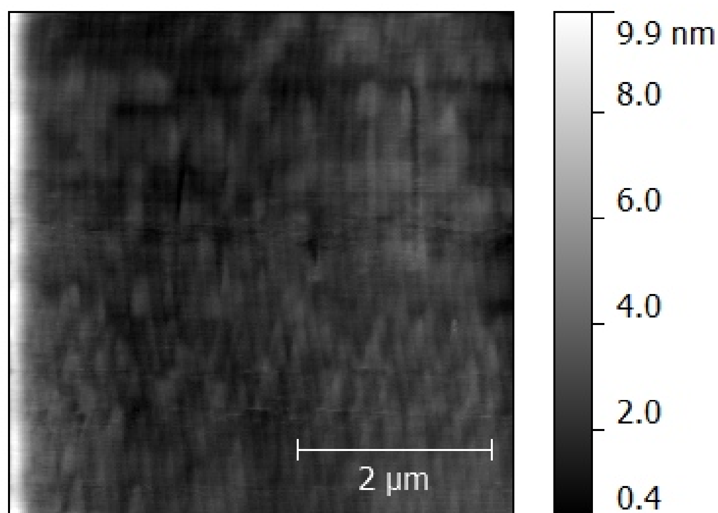

Figure 3.80 AFM image of the Potassium chloride at set point of 2.0V

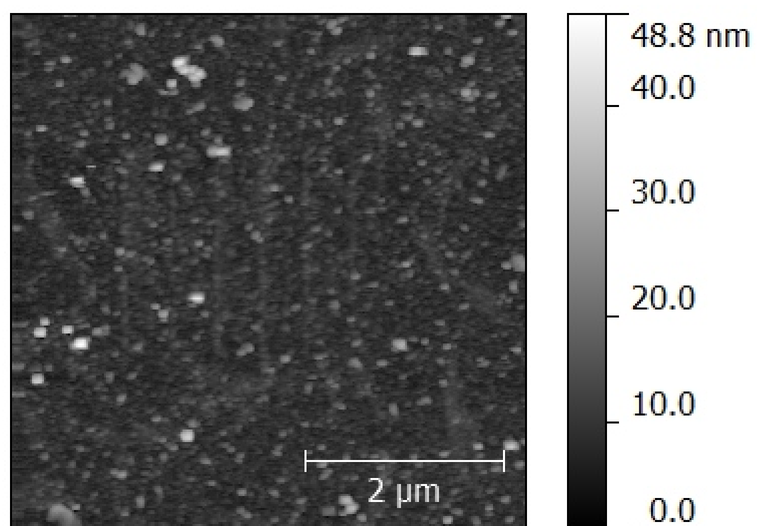

Figure 3.81 AFM image of the Potassium Chloride at set point of 3.0V

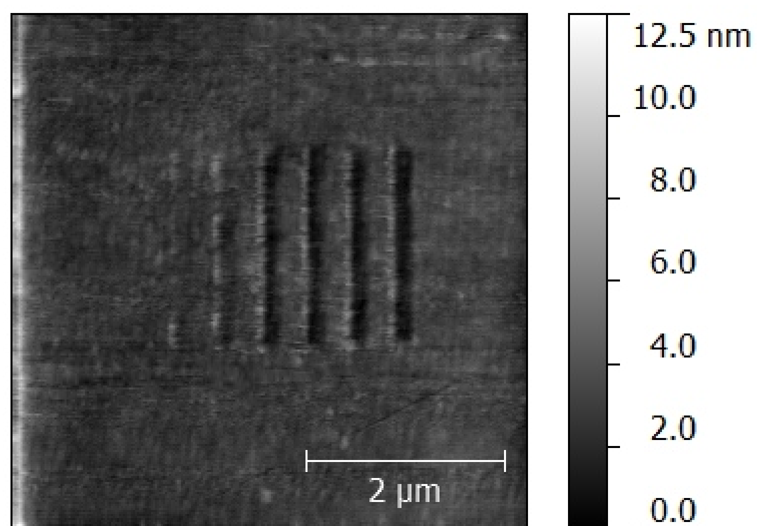

Figure 3.82: AFM image of Potassium Chloride at set point of 4.0V

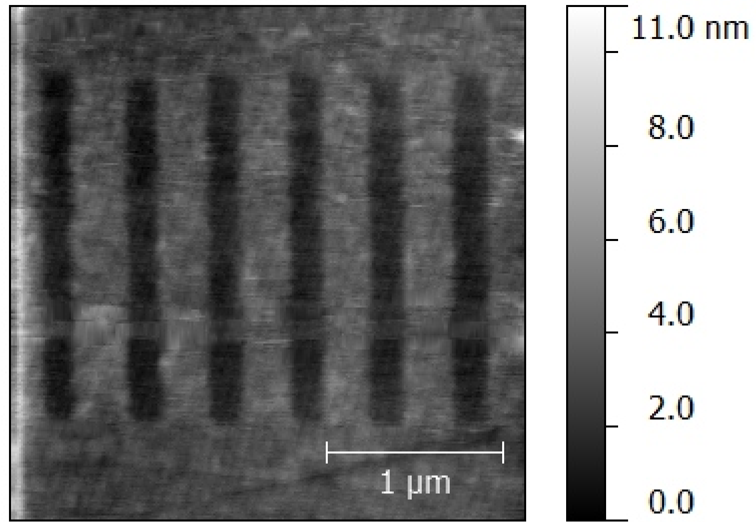

Figure 3.83: AFM image of the potassium chloride at set point of 6.0V

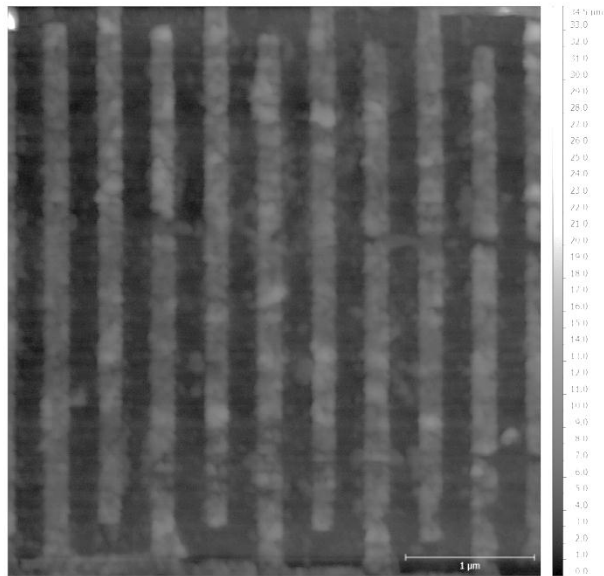

Figure 3.84: AFM image of potassium chloride at set point of 7.0V

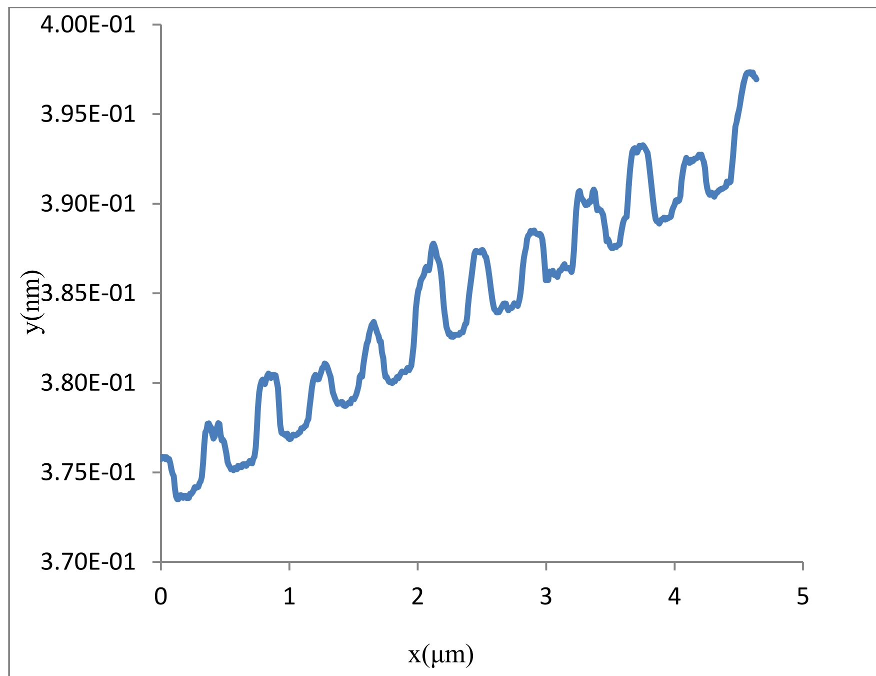

Figure3.85: Profile line of the patterned area in Figure 3.66

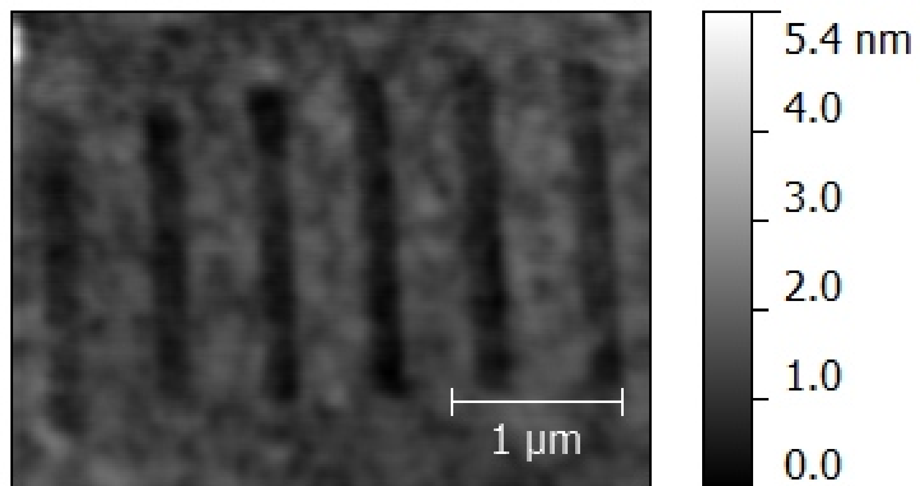

Figure 3.86: AFM image of Potassium Bromide at set point of 2.0V

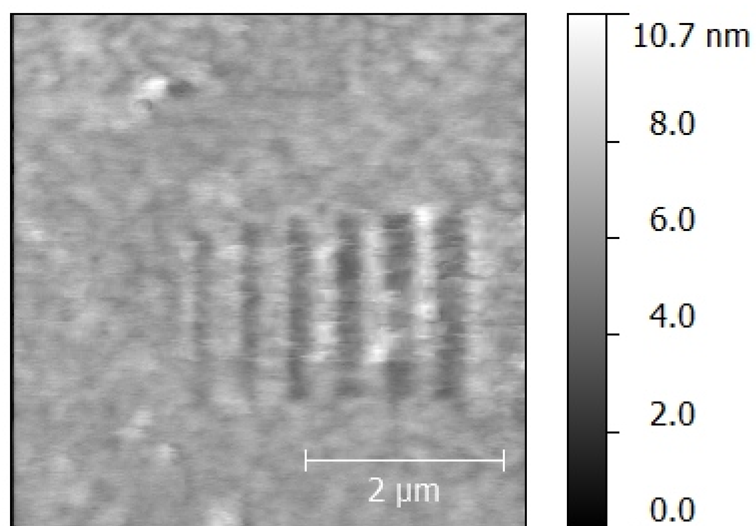

Figure 3.87: AFM image of Potassium Bromide at set point of 3.0V

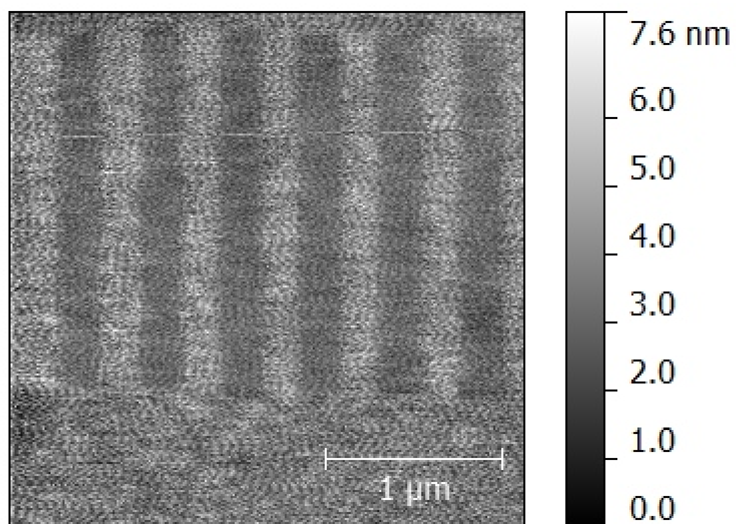

Figure3.88 AFM image of potassium Bromide at set point of 4.0V

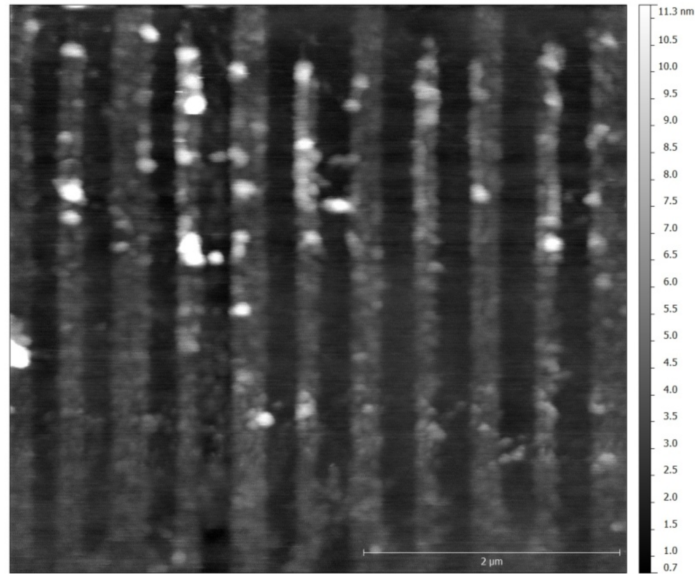

Figure 3.89: AFM image of Potassium Bromide at set point of 4.5V

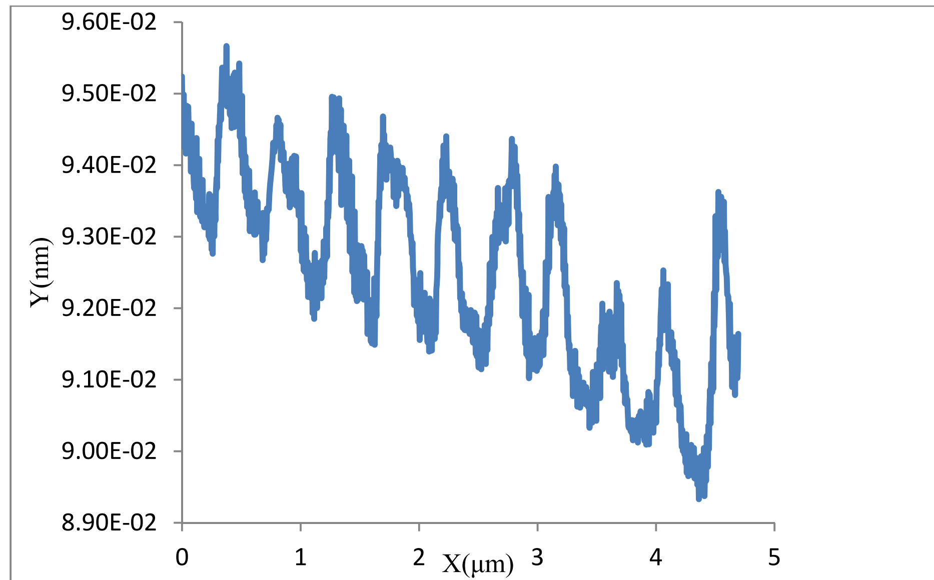

Figure 3.90: Profile line of the patterned area in Figure 3.70

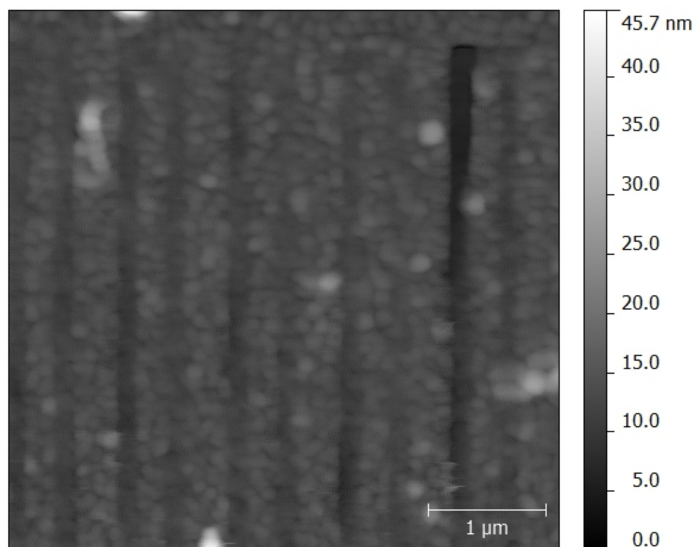

Figure 3.91: AFM image of Potassium Iodide at set point of 0.6V

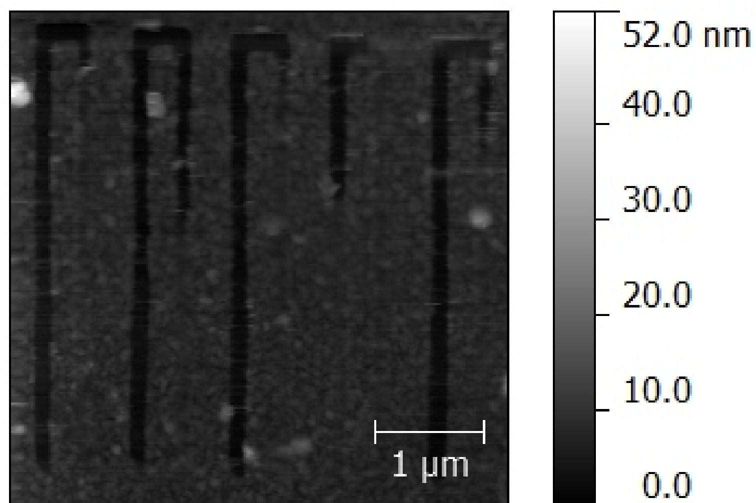

Figure: 3.92 AFM image of Potassium Iodide at set point of 1.6V

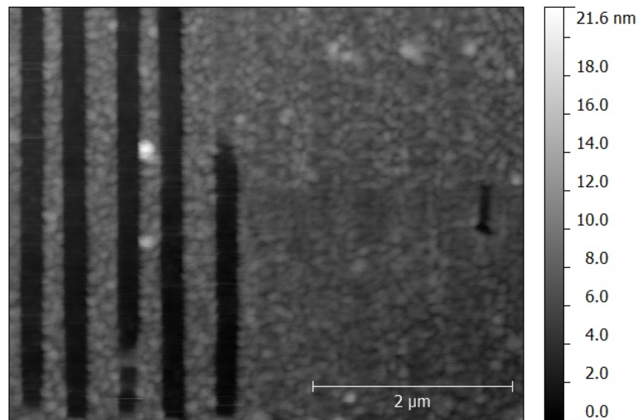

Figure: 3.93 AFM image of Potassium Iodide at set point of 2.6V

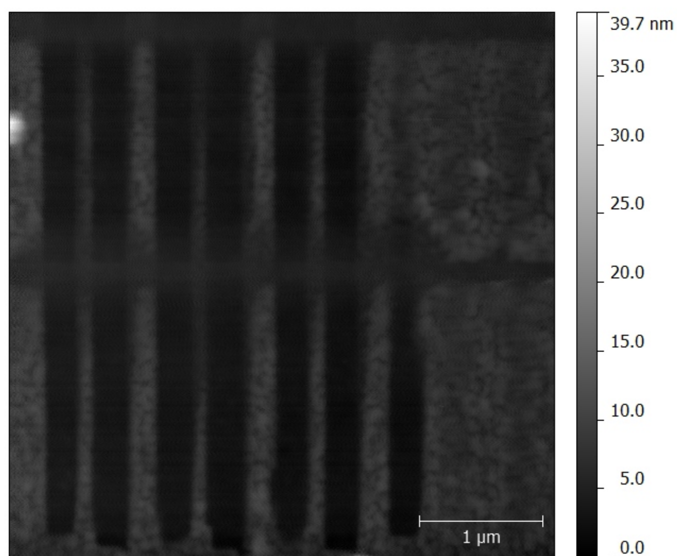

Figure 3.94 AFM image of Potassium Iodide at set point of 3.8V

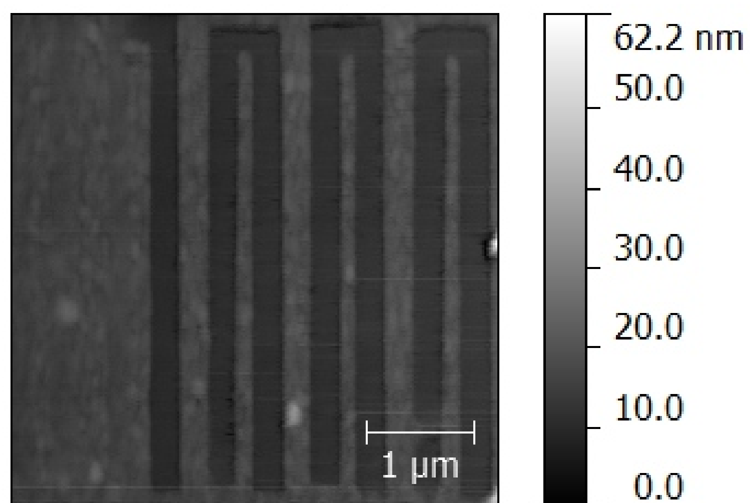

Figure 3.95 AFM image of Potassium Iodide at set point of 4.0V

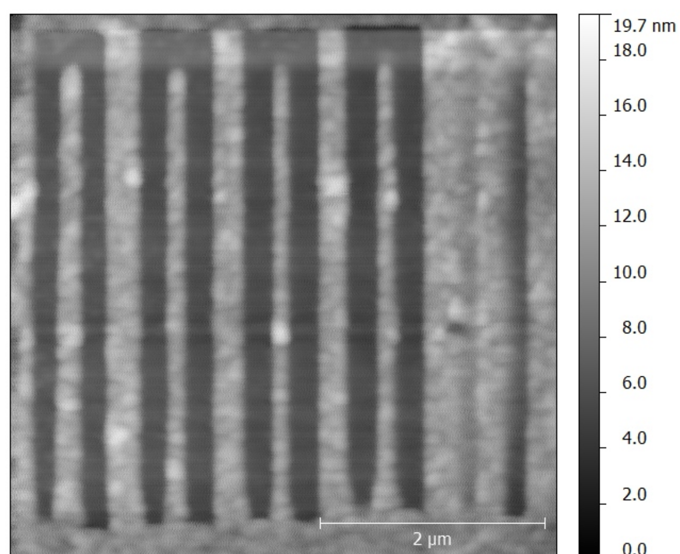

Figure 3.96 AFM image of Potassium Iodide at set point of 5.0V

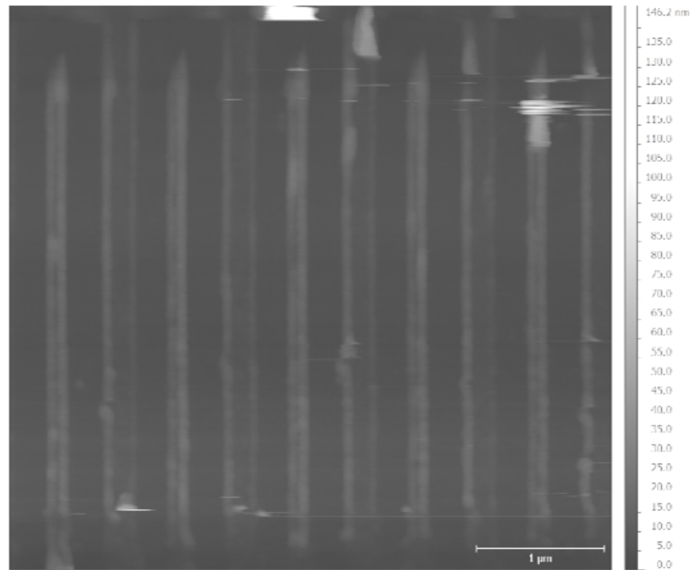

Figure 3.97 AFM image of Potassium Iodide at set point of 6.0V

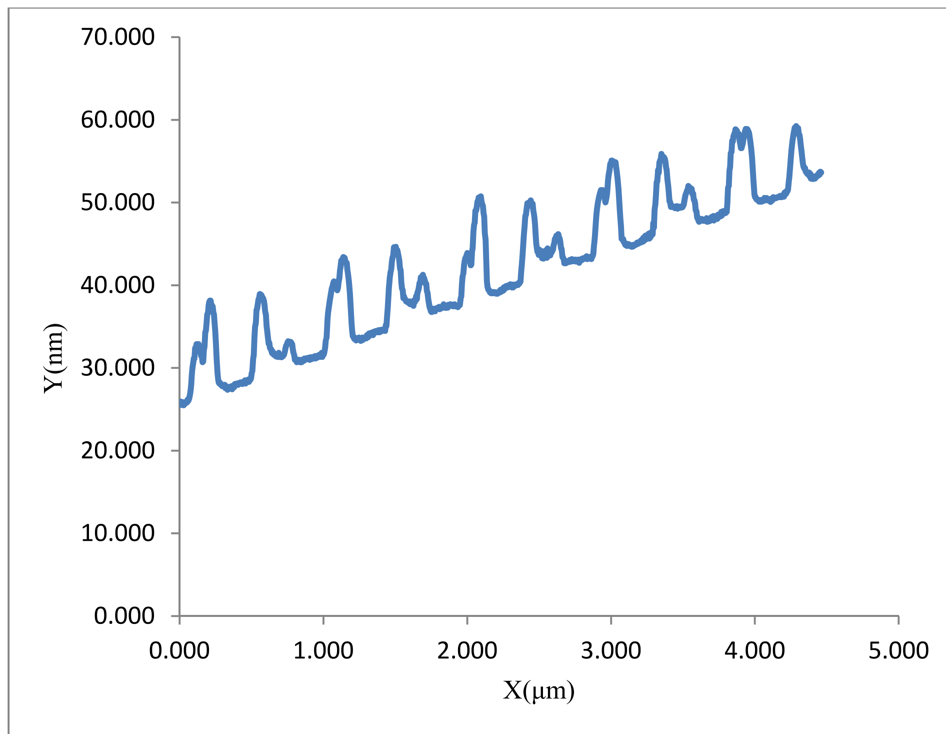

Figure 3.98 Profile line of the patterned area in Figure 3.79

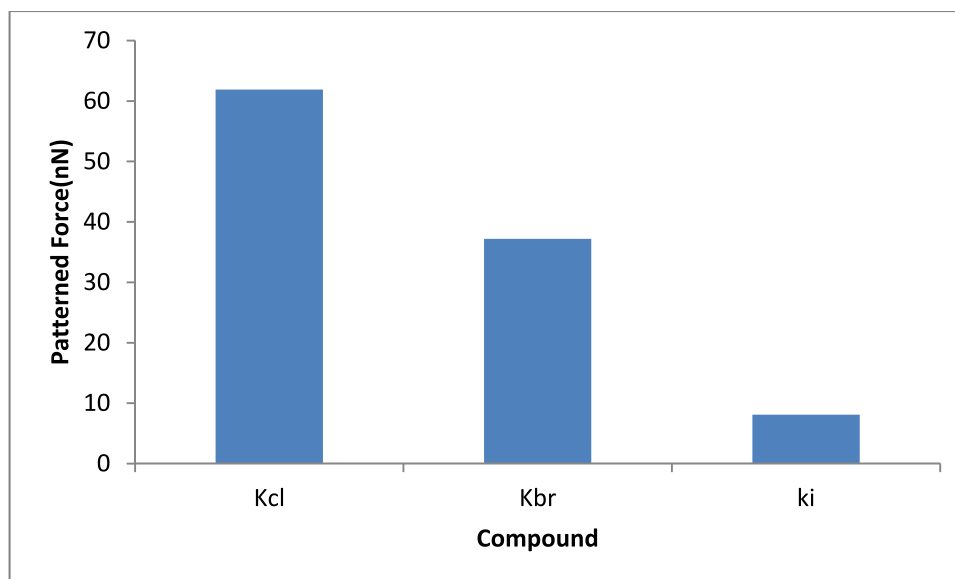

Figure 3.99 Spreadsheet showing a relation between Force taken by the compound to get patterned.

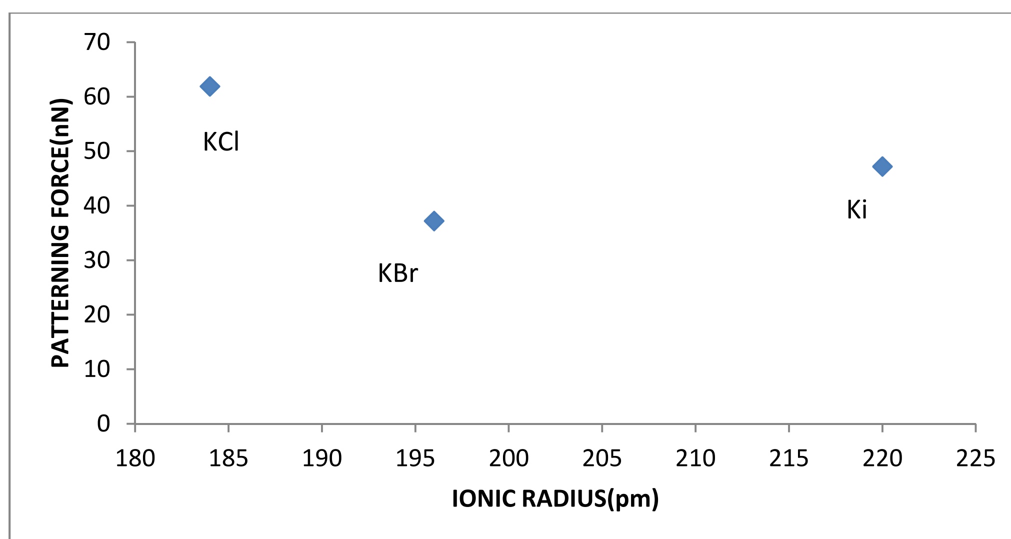

Figure 4.00: Spread sheet showing a relation between the compound and its force and ionic radii.

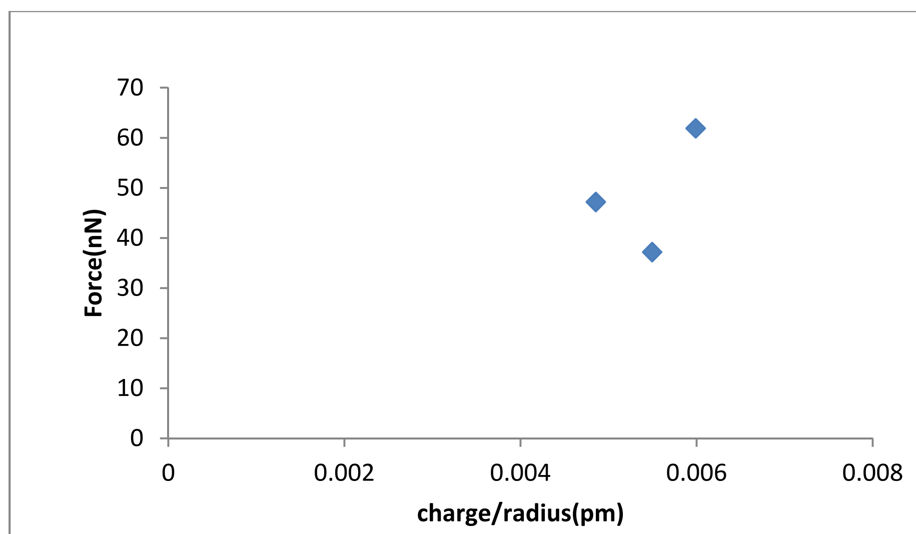

Figure 4.1: Showing a relation between the force and charge/Radius(Pm)

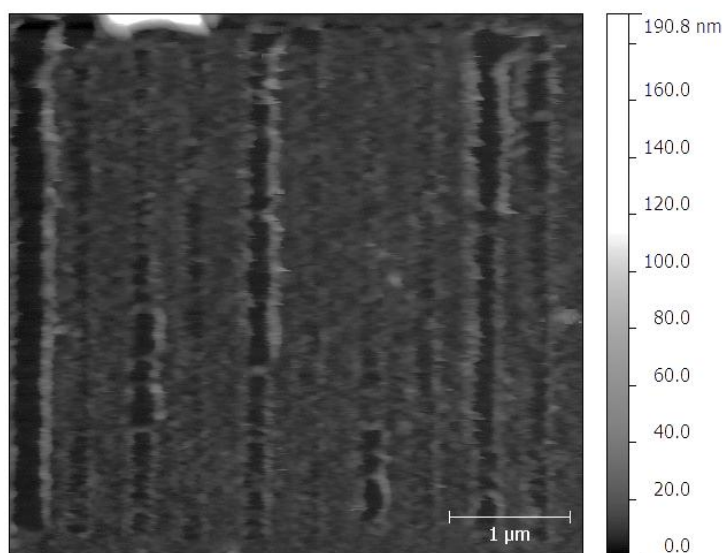

Figure 4.2 AFM image of potassium Hydrogen Phosphate at set point -0.3V

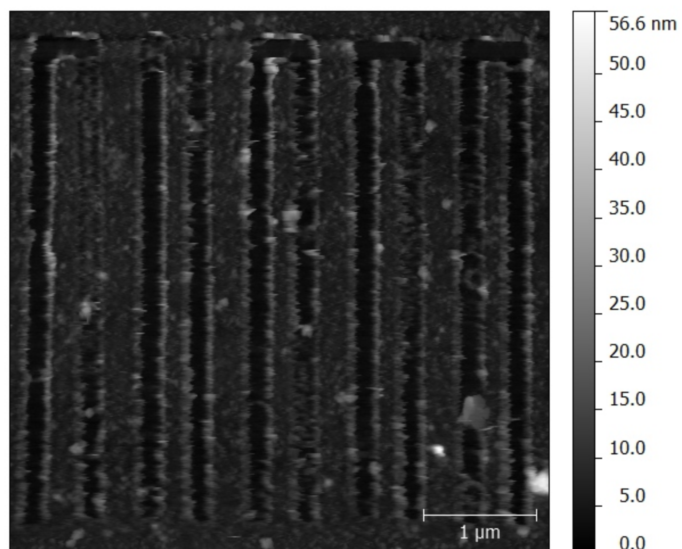

Figure 4.3: AFM image of Potassium Hydrogen Phosphate at set point 2.0V

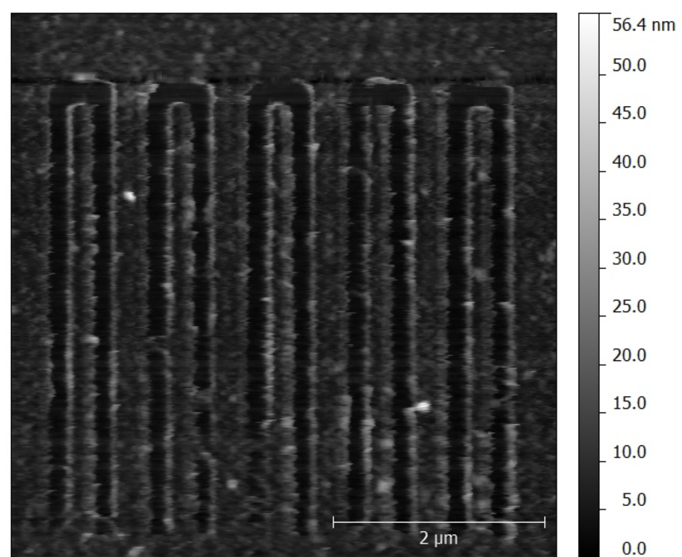

Figure 4.4: AFM image of Potassium Hydrogen Phosphate at set point of 2.1V

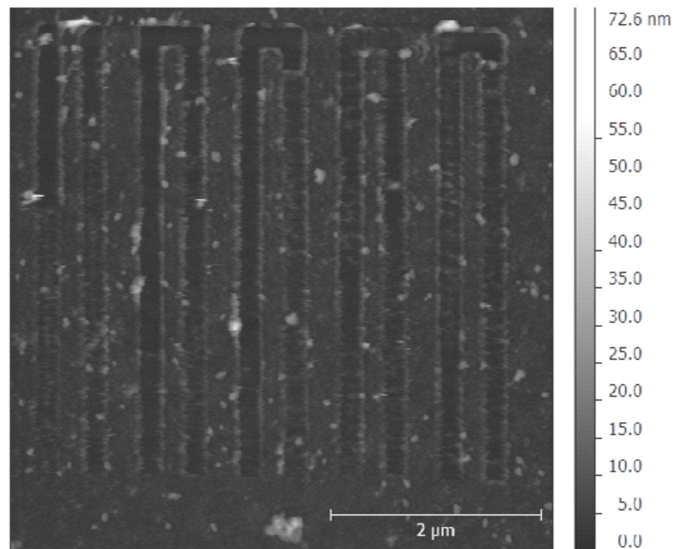

Figure 4.5: AFM image of the Potassium Hydrogen Phosphate at set point of 2.9V

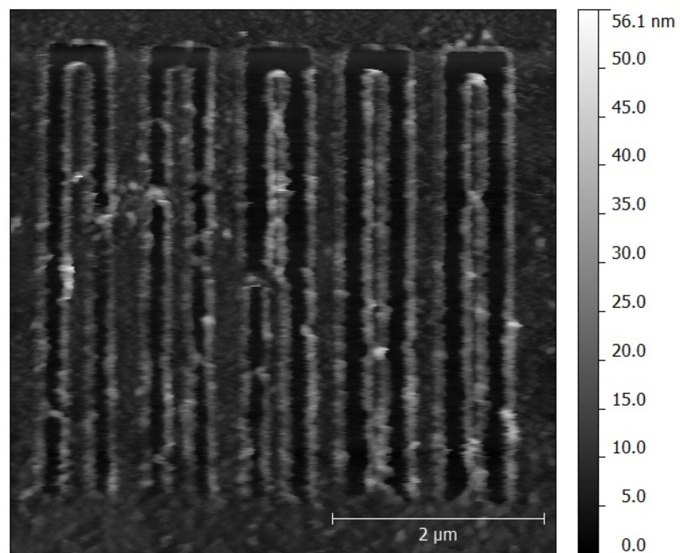

Figure 4.6: AFM image of the Potassium Hydrogen Phosphate at set point of 3.0V

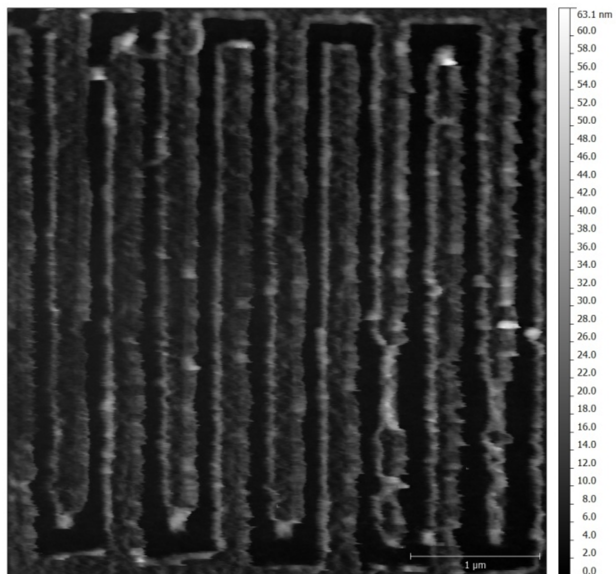

Figure 4.7: AFM image of Potassium Hydrogen Phosphate at set point 3.5V

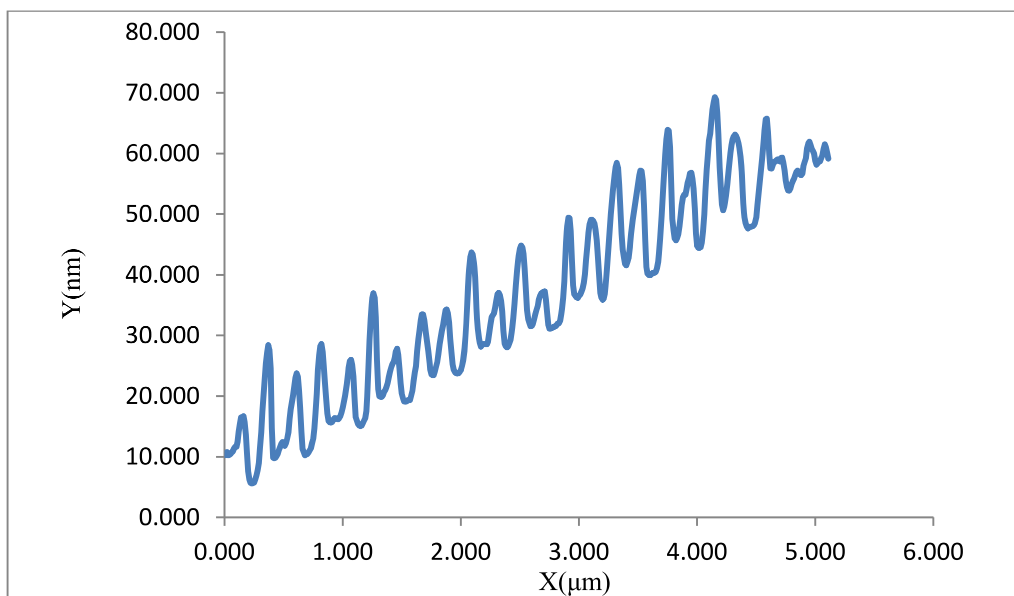

Figure 4.8: Profile line of patterned area in Figure 3.87

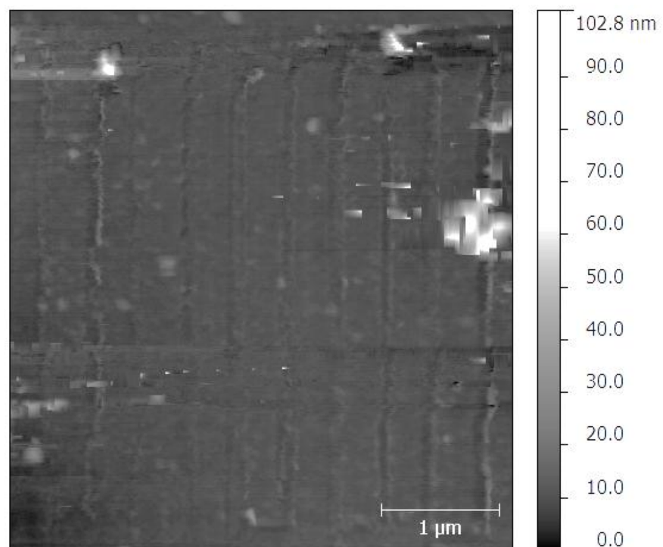

Figure 4.9: AFM image of Potassium Dihydrogen Phosphate at set point 1.0V

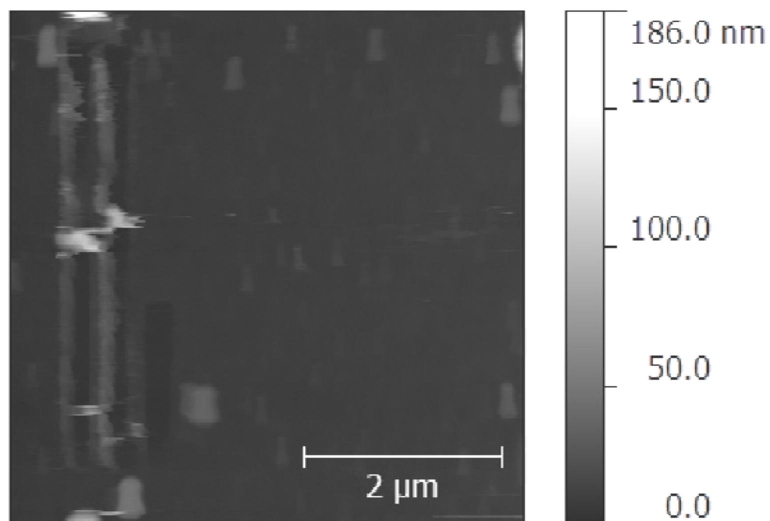

Figure 4.10: AFM image of Potassium Dihydrogen Phosphate at set point 2.0V

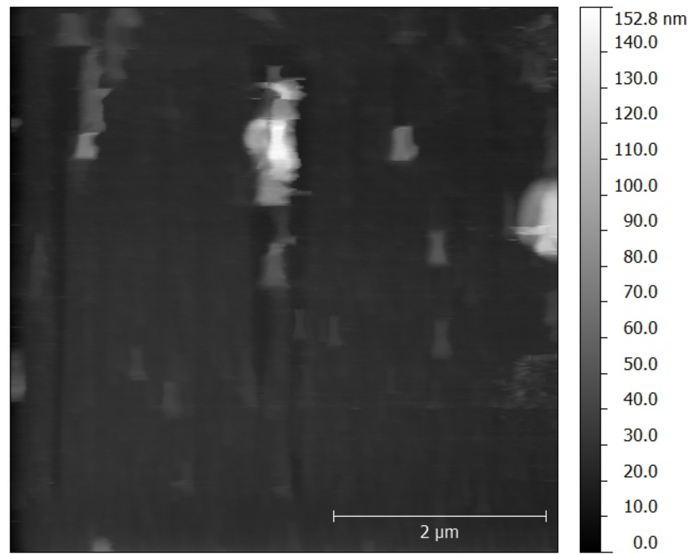

Figure 4.11: AFM image of Potassium Dihydrogen Phosphate at set point 3.0V

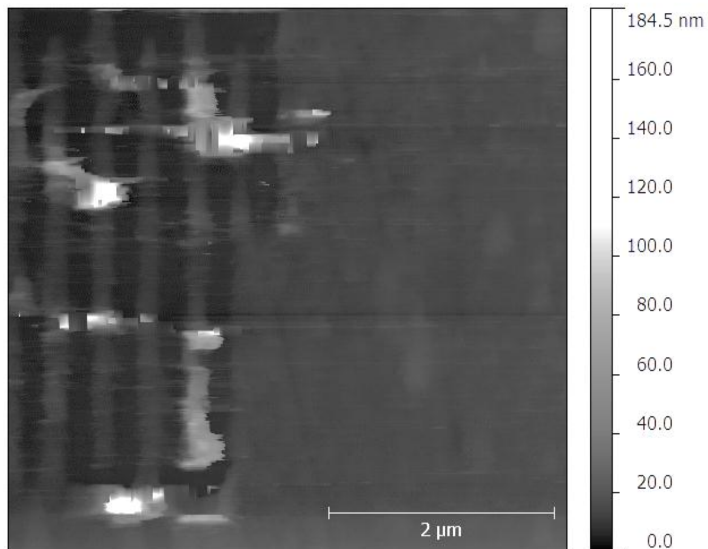

Figure 4.12: AFM image of Potassium Dihydrogen Phosphate at set point 4.0V

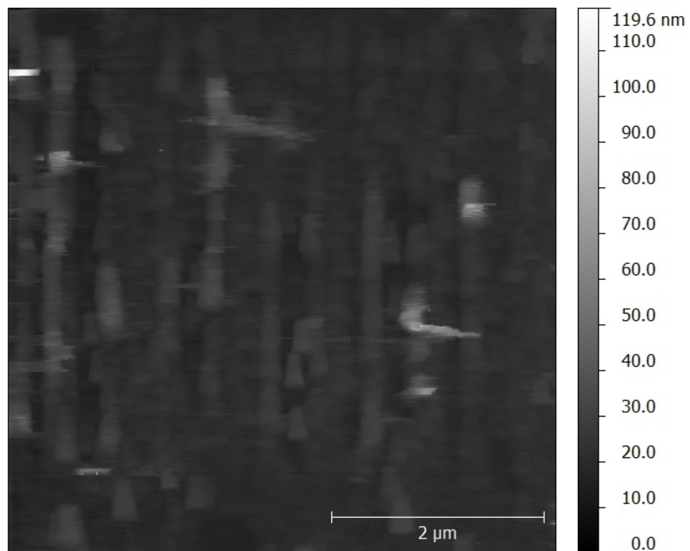

Figure 4.13: AFM image of Potassium Dihdyrogen Phosphate at set point 5.0V

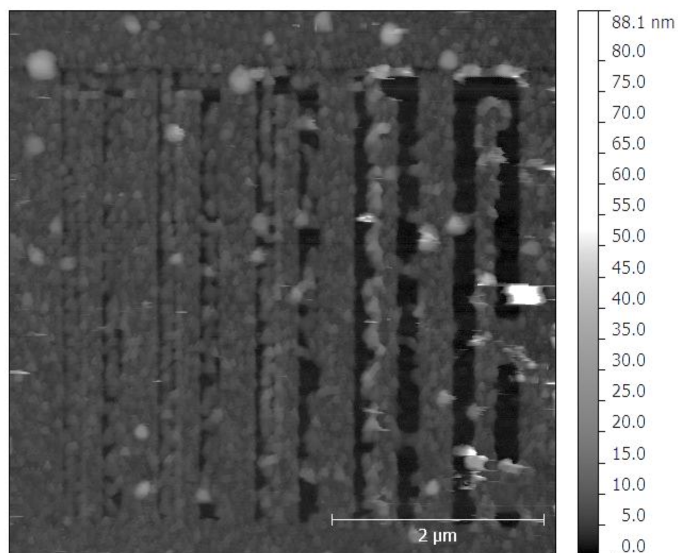

Figure 4.14: AFM image of Potassium Dihdydrogen Phosphate at set point 6.0V

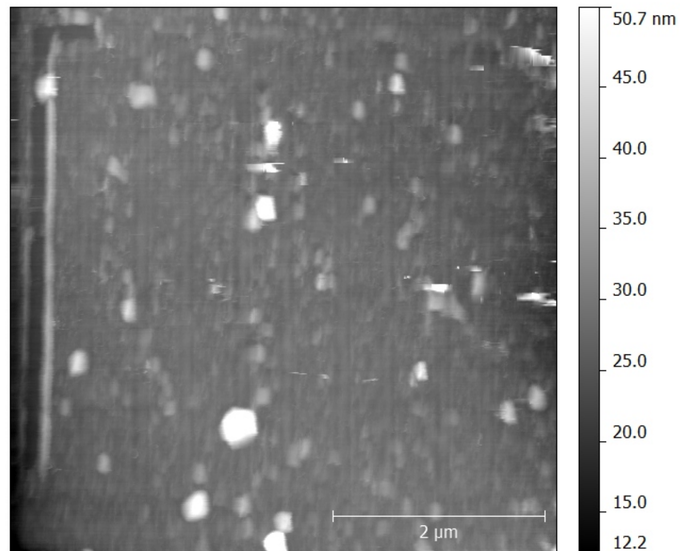

Figure 4.15: AFM image of Potassium Dihdyrogen Phosphate with F tip at set point of 2.0V

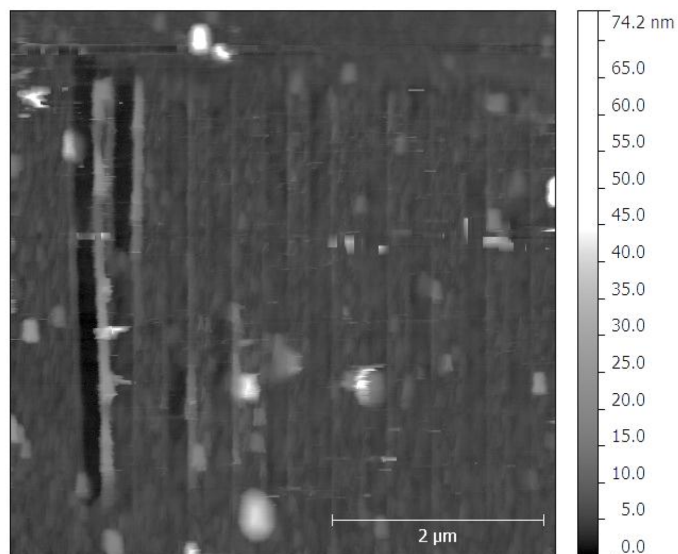

Figure 4.16: AFM image of Potassium Dihydrogen Phosphate with F tip at set point of 2.5V

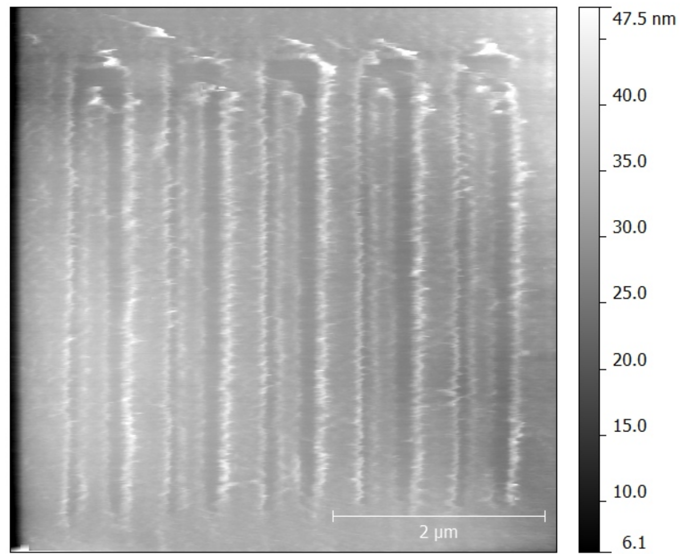

Figure 4.17: AFM image of Potassium Dihydrogen Phosphate with F tip at set point of 3.0V

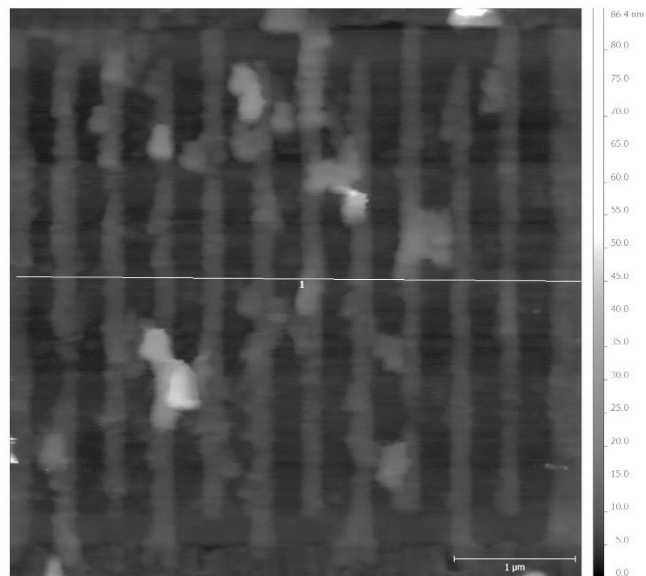

Figure 4.18: AFM image of Potassium Dihydrogen Phosphate with F tip at set point of 3.5V

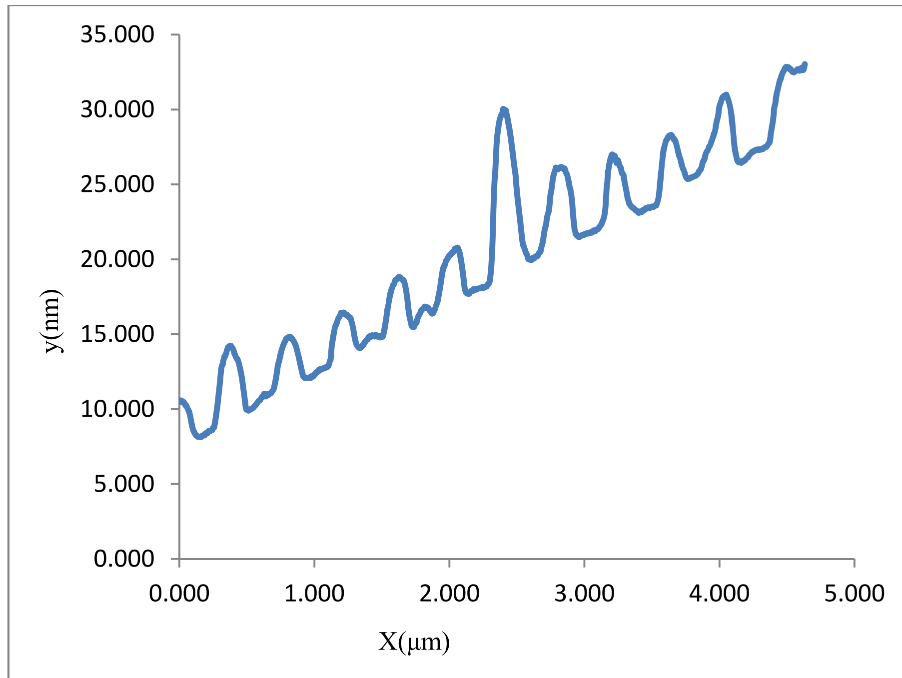

Figure 4.19: Profile line of the patterned area in Figure 3.99

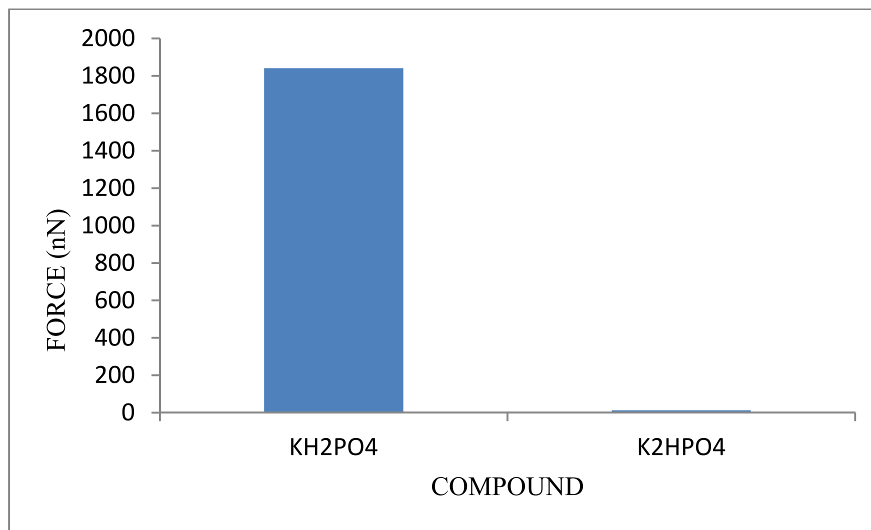

Figure 4.20: Spreadsheet showing a relation between Force taken by the compound to get patterned.

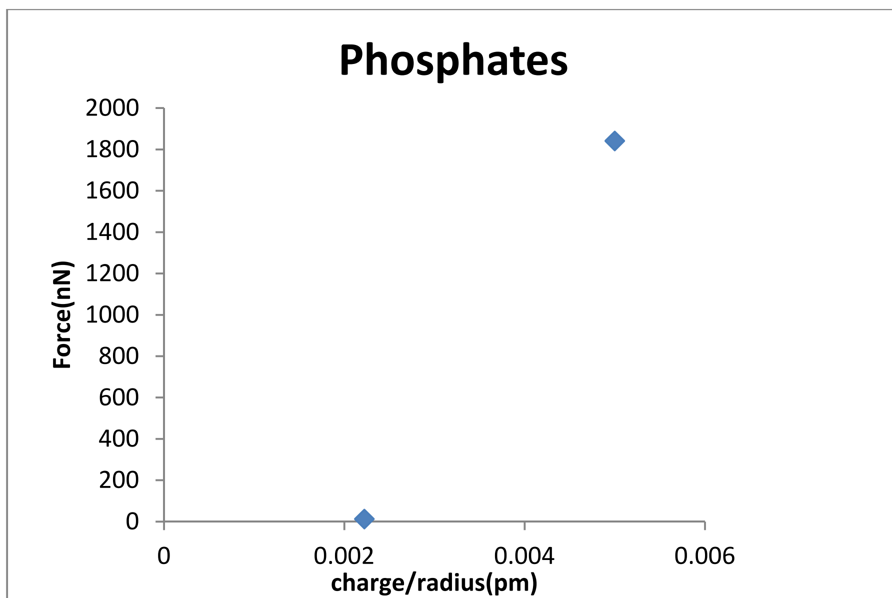

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Figure 4.21 Spreadsheet showing a relation between the force and the charge/radius

CONCLUSIONS

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

- ✓ Various sulphates were investigated to determine the force required for patterning
    - o Sodium Sulphate took a force of 49 nN
    - o Potassium sulphate took a force of 45 nN
    - o Magnesium Sulphate took a force of 744.4 nN
- ✓ Various Halides (Sodium and Potassium) were investigated to determine the force required for patterning
    - o Sodium Fluoride took a force of 8.42 nN
    - o Sodium chloride and potassium Chloride took force of 20.19 and 61.9 nN, respectively.
    - o Sodium bromide and Potassium Bromide took a force of 601.4 and 37.2 nN, respectively.
    - o Sodium iodide and Potassium Iodide took a force of 953.7 and 47.2 nN, respectively.
- ✓ Various Phosphates were investigated to determine the force required for patterning.
    - o Potassium Hydrogen Phosphate took a force of 25nN
    - o Potassium Dihydrogen Phosphate took a force of 43 nN.

- ✓ Patterning force data and pattern quality assessments indicated that the best modifiers to use are Na_2SO_4, NaCl, and KCl.
- ✓ While the pattern quality of $MgSO_4$ and NaBr are excellent, they required too high of a force, which will result in excessive tip wear when patterning over large areas.
- ✓ Case with $MgSO_4$ – Because of its high charge there is a hard interaction with the surface, similar to the native system; therefore, it took a high force to get patterned.
- ✓ Anion size effect: when the ionic radius increases beyond ~200 pm threshold the force required to pattern them also increases to an unacceptably high level.
- ✓ As the anion radius increases, the ability to match the positive surface charge of the PDDA decreases, making larger anions such as iodide (r = 220 pm) poor modifiers.
- ✓ Other anions that may work as well as sulfate (r = 258 pm) and chloride (r = 184 pm) include:
  - NO_3^- (r = 179 pm)
  - ClO_3^- (r = 171 pm)
  - BrO_3^- (r = 154 pm)

FUTURE WORK

- ✓ Modeling of surface interactions
- ✓ Other modifications to the methods
  - ✓ The effect of patterning done by controlling the tip speed.
  - ✓ Patterning under solution
- ✓ 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.

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