Stony Brook University

Blend Polymer Masks for Transfer of Nanometer-Scale Patterns into Ti surface

A Thesis Presented

by

Yingjie Yu

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in Partial Fulfillment of the

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Abstract of the Thesis

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The purpose of the project is to produce high resolution pattern on titanium substrate. As we known, titanium, as an important material, has been widely used in medicine area, such as dental and orthopedic implants. Moreover, their integration in the bone is very good without fibrous interface layer. However, titanium and its alloys have certain limitations. It is possible that metal ions are released to the human environment. As a result, the release of these elements may lead to many problems such as local irritation of the tissues. Cell and tissue responses are influenced by the surface topography or roughness of the implants. In order to improve the biological, chemical, and mechanical properties, many surface treatment techniques are used. In this project, nanolithography is used to fabricate high resolution pattern on the titanium substrate. The phenomenon of phase segregation for block polymer is an important way for us to utilize to produce big height variation, which is crucial for us to construct high resolution pattern.

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Chapter 1 Introduction

1.1 Motivation and Background

With the development of bio medicine, implantation technology has already been widely used. To meet the requirement of implantation, materials used for implant applications must have good mechanical strength, high chemical stability, excellent corrosion resistance and biocompatibility [1,2]. Titanium, as a common material extensively used in implantation, meet the requirement of this process. In bone anchoring systems, such as dental and orthopedic implants titanium is extensively used. In table 1.1 [3] gives the mechanical properties of various materials used for implant applications. We can see that titanium exhibits mechanical properties similar to bone. Moreover, titanium has a significantly lower density than other metallic biomaterials, which means that the implants are much lighter than similar item made by other alloy. Therefore, it is true that titanium can be alternative for bone, however there are some concerns regarding the use of titanium. Some issues such as the long-term stability of hip joint prostheses [4] and healing response.

Altering the titanium surface can solve these problems as surface parameters play an important role to obtain effective implant-tissue interaction. Presently, a common way to improve the osseointegration is the coating of titanium surface with hydroxyapatite. Although they are commercially popular, plasma processes create thick coatings have various phases of mixed crystallinity [5]. However, this thick coating leads to delamination and dissolution of phases [6]. Therefore, a possible way to create nice pattern on titanium surface is important for the application of implantation.

Material	Elastic modulus (GPa)	Yield strength (GPa)	UTS (GPa)
Pure Ti	105	692	785
Ti–6Al–4V	110	850–900	960–970
Ti–13Nb–13Zr	79	900	1030
Co–Cr–Mo	200–230	275–1585	600–1795
Stainless steel	200	170–750	465–950
Bone	1–20	–	150–400

Table 1- 1 Mechanical properties of several materials.

To make a high resolution pattern on titanium substrate, lithography is a good way to create uniform and high resolution pattern [7]. However, it is widely recognized that further extension of optical lithography to smaller dimensions will be accompanied with the problem of rapid increasing cost and difficulty. Because of this, finding an alternative patterning methods is necessary. Block copolymer lithography, which uses self-assembled microdomains of block copolymers in thin films, can make patterns with nano length scales by a simple process and easy way [8].

In this project, a promising way to make a high resolution pattern on titanium substrate is proposed, and we will use different characterization ways to check the quality of our pattern on titanium substrate.

1.2 Objectives and Methodology

To make a nice pattern, we have to find a proper way to do lithography on titanium. After reviewing other articles, we found out that there are a lot of lithography way can make pattern on different substrate. Such as photolithography and electron beam lithography. In this project, we will us ion projection lithography to etch block polymer surface to achieve high resolution pattern. First, we will etch the surface on the silicon substrate. Then, after obtaining nice pattern on silicon substrate, we continue to tech the polymer thin film surface on the titanium substrate.

After producing pattern on substrate, we need to see the morphology of the pattern, and analyze the data to see whether we achieve high resolution pattern on the substrate. Therefore, Atomic Force Microscopy (AFM) is a reasonable choice for us to analyze the surface condition of our sample.

1.3 Thesis Structure

Chapter 2 reviews existing approaches developed by other people to create nice patterns. There are several ways to do lithography, such as nanolithography, photolithography, and electron lithography.

Chapter 3 presents the material we used in the experiment, and the equipment we used to make thin film and character the material such as AFM and ellipsometry. In addition, in this section, the specific experiment procedure is illustrated.

Chapter 4 presents the experiment result we obtained. Different AFM images of the pattern are exhibit in this section. Moreover, we will analyze the data we obtained in this experiment to find out the best sputtering pattern.

Chapter 5 presents the conclusion that we made based on our experiment. In addition, a promising way to fabricate nice pattern on titanium are also provided.

Chapter 6 presents the future work we can do to improve the quality of our pattern. Besides, we can do more experiment in practical bio environment to test our pattern, and we will improve the quality of pattern by changing the experimental condition.

Chapter 2 Literature Review

Several papers were already published by various authors concerning lithography. Nanoimprint lithography, a high-throughput, low-cost, nonconventional lithographic method proposed and demonstrated recently, has been developed and investigated further. Moreover, lithography on self-assemble block polymer is also study.

2.1 Nanoimprint lithography

One of the major obstacles in developing nanostructures is the lack of a low-cost, high-throughput manufacturing technology. Especially, for structures with a size below 0.1 mm, this problem is relatively serious and obvious. Because of this condition, numerous technologies are under development to solve this problem [9]. Nanoimprint lithography, as a new technology, has achieved 25 nm feature size, which is very sophisticate for normal application. Further experimental research proves that the maximum resolution of nano-lithography could be 10 nm, the imprint process is repeatable, and the mold is durable [10].

2.1.1 Principle of nanoimprint lithography

Nanoimprint lithography has two basic steps as shown in Fig. 2.1. The first is the imprint step. A nanostructure mod is pressed into a thin resist on a substrate. After that we remove the mold on the surface [11]. After this step, nanostructures were duplicated on the mold in the resist film, which means the imprint step creates a thickness contrast pattern in the resist. The second step is the pattern transfer where an anisotropic etching process, such as reactive ion etching (RIE), is used to remove the residual resist in the compressed area [12]. Through this step, the

thickness contrast is transferred into the entire resist. During the imprint step, we have to heat the resist to a temperature above its glass transition temperature. It is well known that, under this condition, the resist, which is thermoplastic, becomes a viscous liquid and can flow. Therefore, it can be readily deformed into the shape of the mold.

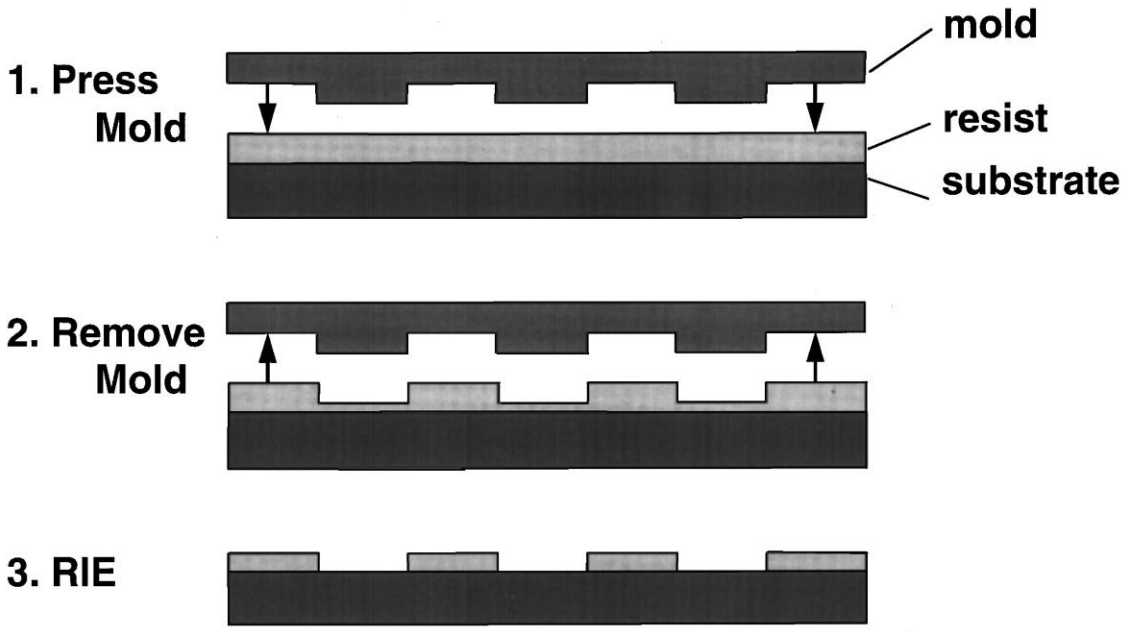


Figure 2- 1 Schematic of nanoimprint lithography process

Unlike conventional lithography methods, imprint lithography itself does not need to use any energetic beams. Therefore, nanoimprint lithography's resolution is not limited by the effects of wave diffraction, scattering in a resist, and backscattering from a substrate which is a common problem for conventional method. In addition, imprint lithography is basically different from stamping using a monolayer of self-assembled molecules [13]. Therefore, imprint lithography is more like a physical process rather than a chemical. It is entirely possible that in the future, the mold used in imprint lithography can be made using a high-resolution but low-throughput

lithography, and then imprint lithography can be used for low-cost mass production of nanostructures.

2.1.2 Experiment process

In this experiment, Stephen Y. Chou et al use silicon dioxide and silicon as the mold materials [14]. Other materials such as metals and ceramics could also be used. After preparation, they got the mold which patterned with dots and lines with a minimum lateral feature size of 25 nm using electron beam lithography and RIE. Poly methyl methacrylate (PMMA) was primary material used as resist in this experiment.

According to compare with different materials, they found out that the PMMA exhibited the excellent properties for imprint lithography. First of all, PMMA has a relatively small thermal expansion coefficient of 5×10^{-5} per ℃ and a small pressure shrinkage coefficient of 3.8×10^{-7} per psi,[9] which is very suitable for imprint [15]. At the same time, we also add mold release agents into the resists in order to reduce the resist adhesion to the mold. The experiment condition, like the pressure and temperature, for the imprint process depend on the material used in resist. For PMMA, which has a glass-transition temperature of about 105 ℃, the temperature used in their experiments is between 130 and 170 ℃, and the pressure is from 600 to 1900 psi [16]. Because in that temperature and pressure condition, the PMMA thermal shrinkage is less than 0.8% and the pressure shrinkage is less than 0.07%. So the shape of the PMMA should be similar to that of the mold. In order to reduce air bubbles, the experiment condition should be kept in vacuum. The gas used in the RIE pattern transfer, which also depends on the resist used, was oxygen for PMMA.

2.1.3 Results and discussion

Various nanostructure were obtained by PMMA imprinting [18]. For example, they create a structure that possesses 25 nm diameter hole, and a 120nm period. Figure 2.2 presents a scanning electron micrograph of imprinted PMMA strips before RIE. In the figure 2.2, the strips, which are 70 nm wide and 200 nm deep, exhibit very smooth and perpendicular sidewalls, and nearly 90 °corners [19]. In order to allow for test of side walls, the spacing between the strips were intentionally made large. As shown later, curvature of the shape in the mold creates the small bend at the end of the PMMA strips.

In order to compare the imprinted resist profile with the profile of the original mold features, we test the mold using a scanning electron microscope (SEM) as shown in Fig. 2.3. The PMMA morphology presented in Fig. 2.2 obtained from the closed end of the mold fingers; therefore, it is not reasonable to compare the mold shape and the PMMA profile [20]. Nevertheless, comparison of the general characterizations, such as the line width, heights, and slight bending at the end of each line, proved that the PMMA profile are similar to the mold.

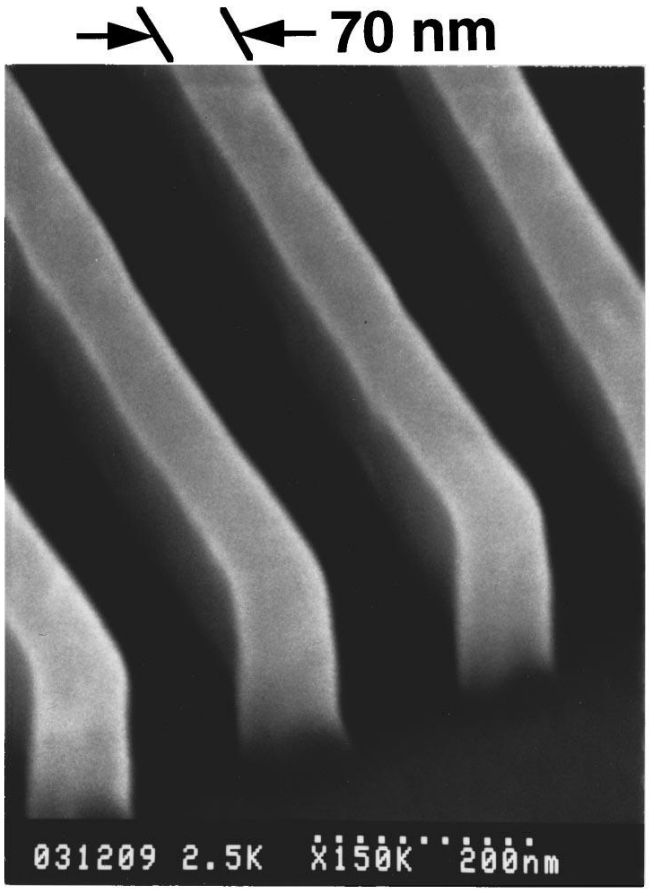


Figure 2- 2 SEM micrograph of a perspective view of strips formed into a PMMA film by imprint.

According to Stephen Y. Chou et al, the minimum feature size of imprint lithography is related to the minimum feature size on the mold [21]. Hence if we obtain the polymer that exhibit sufficient mechanical strength, imprint lithography should be able to produce 10 nm feature size in the polymer [22]. In addition, process repeatability and mold durability is very important for manufacturing technology. To test that, they used same mold to imprint PMMA over 30 times to examine the mode, and no noticeable change has been found. Actually, over 30

times imprinting is still not enough to be considered a good repeatability, they will do more process to test the imprint.

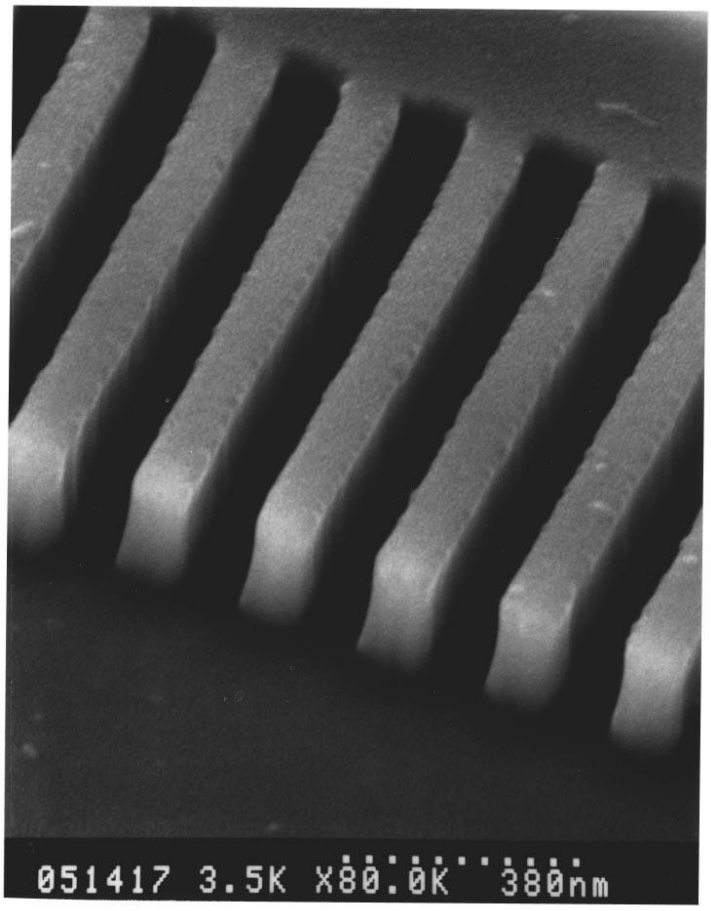


Figure 2- 3 SEM micrograph of the mold that was used to imprint the PMMA strips shown in Fig. 2-2

In conclusion, nanoimprint lithography is a very promising way to create micro nanometer feature size and 80 nm pitch, perpendicular and smooth sidewalls, nearly 90 °corners in a single print [23]. With further development, imprint lithography can become the technology for manufacturing nanostructures, and can have a significant impact in many areas such as integrated circuits, biology, and chemistry.

2.2 Surface patterns from block copolymer self-assembly

Block polymer material, which is an important polymer, spontaneously from patterns by a minimization of free energy [24]. This process is known as microphase separation. Because of the distinct property of block polymer, people use this self-aligned polymer for high resolution lithography. Self-assembly provides enhancements by controlling material nanostructure. Many researches about using self-assembly to pattern individual elements of devices and circuits has been reported.

The first experimental demonstration of self-assembled block copolymer pattern to lithographically defined surface topography used thin films of sphere-forming PS-b-PVP (Polystyrene: Polyvinylpyridine) [25]. We can see that lithography on block polymer is a possible way to obtain high resolution pattern.

Chapter 3 Materials and Methods

In this chapter, the experimental procedure will be presented specifically. In this experiment, we use spin cast to make polymer thin film for pure polymer and blend polymer. After that, we will use ellisometer and AFM to analyze the surface of pattern.

3.1 Experimental Materials

Polystyrene (PS) (Mw=123,000), Poly (methyl methacrylate) (PMMA) (Mw=120,000), Titanium, Silicon Wafer

3.2 Experimental Equipment:

Southwest Science Hotplate, Branson 3510 sonicator, photo-resist spinner (Headway Research Inc, 1-PM107D-R485), Gatan precision ion polishing system (Model 691), Automatic Force Microscopic (AFM), Rudolph three wavelength Ellipsometer, High Temperature Oven,

3.3 Experimental Step

3.3.1 Solution Preparation

Polystyrene solution (PS) were prepared of 4 wt. % and 7.5 wt. % PS at a concentration of 40 mg/mL and 75 mg/ml respectively, 7 wt. % Poly (methyl methacrylate) PMMA at 70 mg/mL, both polymers were dissolved in toluene. To obtain different blend nanocomposites, we prepared solutions of varying concentrations of PS to PMMA. The ratios of PS:PMMA were as following: 1:1, 1:3, and 3:1 (all at 4 wt. % of polymer to solvent). All solutions contained a stir

bar and were placed on a hot plate for 20 minutes on the Southwest Science Hotplate at a speed of 4 and heat level of 1 to dissolve solutions.

3.3.2 Substrate preparation

We cleaved silicon into 1cm x 1cm squares and then sonicated the samples in the Branson 3510 sonicator with the heat off for 20 minutes, first with distilled water and then menthanol. Organic contaminants were removed with a 3:1:1 ratio of H_2O:H_2O_2:NH_4OH to create hydrophilic silicon, then the beaker with this cleaning solution was left on the hot plate to boil lightly for 15 minutes. Subsequently, inorganic contaminants were washed off using a 4:1:1 ratio of H_2O:H_2O_2:H_2SO_4. Hydrofluoric acid (HF) was used in a 1:10 ratio (10 parts water) in a petri dish to remove the clean oxide layer, creating hydrophobic silicon.

3.3.3 Evaporate Ti onto Si wafer

In order to deposit Titanium layer onto the silicon wafer, we can use evaporation machine to condense metal. Evaporation involves two basic processes: a hot source material evaporates and condenses on the substrate. It resembles the familiar process by which liquid water appears on the lid of a boiling pot. However, the gaseous environment and heat source are different.

3.3.4 Spin-casting thin films

Thin films were prepared on specific substrates by using a photo-resist spinner (Headway Research Inc, 1-PM107D-R485). After putting sample into HF solution, we spun this sample for 45 s at 2500 rpm to create polymer thin film.

3.3.5 Anneal sample

The spin-cast films we made possess nonequilibrium surface, in order to change the thin film from unstable condition to stable condition, we have to anneal sample at 180℃ for 12 hours.

3.3.6 Ellipsometry

After spinning cast pure polymer solution to make thin film, with the use of the Rudolph Research ellipsometer, we were able to determine the thickness of our samples in angstroms. During each reading delta and psi parameters were kept constant ~60 and ~50 respectively. Indexes of refraction were variable; PS has an n value of 1.589 and PMMA has a real n value of 1.489. Knowing the n values is necessary for determining thicknesses of pure PS and PMMA samples.

3.3.6 Sputtering

Gatan precision ion polishing system (Model 691) was used to etch polymer thin film. The ion mill contains argon gas which is ionized by a strong magnetic field within the mill. A 3mm x 3mm sample is placed on a stage which is lowered into a vacuum setting and rotated as argon ions in different voltage are accelerated from two ion guns kinetically etch away the sample. The stage is rotated at 3.0 rpm and the maintained pressure is 7 x 10 ^-4 torr. Samples were sputtered for different time.

3.3.7 Removing polymer on sputter sample

In order to get the nice pattern, we have to remove the polymer on the surface. After sputtering, we have to put our sample into the high temperature oven at 700 ℃ for 30 minutes. Because the melting point of PS and PMMA is 240 ℃ and 160 ℃, and the melting point of Titanium is 1668 ℃, under this temperature, we can make sure PS and PMMA is melted and Titanium is well kept. After removing polymer, we have to clean surface of the sample for future use. Normally, we use Isopropyl alcohol clean first, then we use acetone to rinse the sample, at last, we use DI water to clean. Then we use nitrogen gas to dry sample for future characterize.

3.3.8 Atomic Force Microscopy

This imaging technique allowed us to gain greater understanding of the surface and polymer/polymer interaction. The AFM was used in both contact and tapping mode to take topography, friction, and phase scans. Images were analyzed to characterize thin film morphology and note differences in polymer behavior among the different samples. Using Nanoscope programming, we can analyze the image obtained from AFM to know the information about our sample, such as the thickness difference, morphology, polymer dispersion.

Chapter 4 Result and Discussion

4.1 Optimization of sputtering condition

The sputtered rate is governed by several factors, such as incident angle, sputtered voltage, and sputtered current. Therefore, in order to compare the experiment result, we have to set an optimized experiment condition for all of our sputtered experiment.

According to J.Jerome's paper [26], in figure 4-1, we can see no further improvement occurs when the incident angle is increased to 30°. So we select 30° as incident angle in our experiment. Since sputtered rate is strongly related to voltage, the relationship between sputtered rate and voltage is necessary for our study.

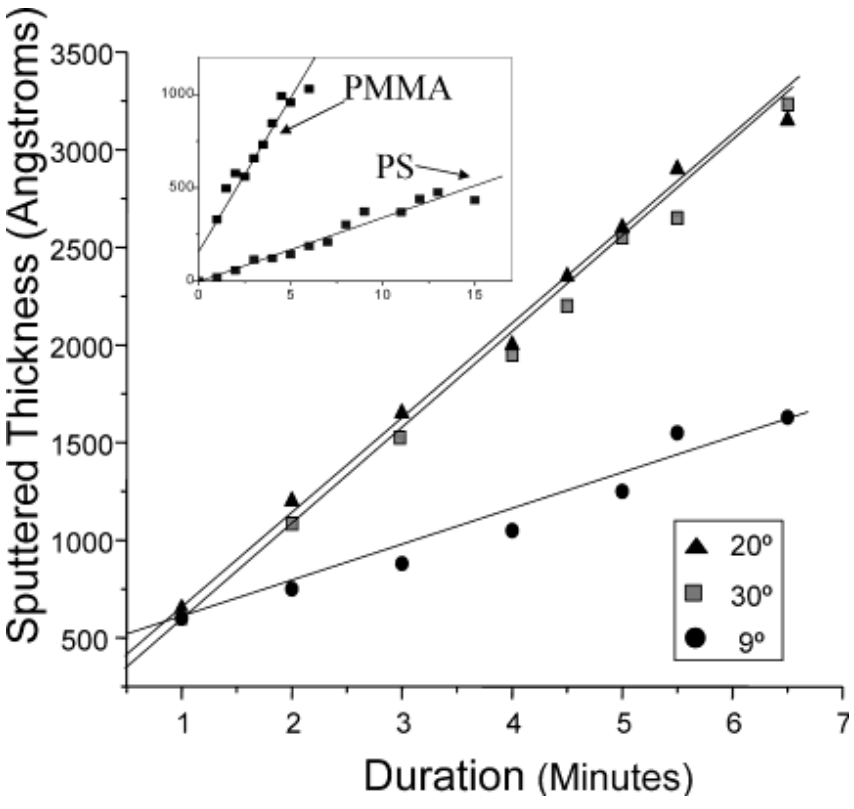


FIgure4- 1 Sputtering rate as a function of time of an Ar ion beam. The different traces correspond to different incident angles. Inset: comparison of the thickness vs time for 350 nm PMMA and PS film sputtered at an incident angle of 35 °

6 samples spun cast of PS with concentration of 40 mg/ml were used in this experiment. Each of these samples will be sputtered for 1 minute under a current of 0.5 mA. After sputtering, the thickness of the films was measured with a Rudolph three wavelength ellipsometer. In figure 4-2, we can see that the sputtered thickness of thin film as a function of sputtering voltage. It is clearly that the sputtered thickness increased with the voltage increasing. Furthermore, from 2kV to 4 kV, the sputtered thickness changed dramatically. In this study, we want to find a moderate voltage to sputter our sample. This voltage should not be too large to observe the thickness change, or too small to sputter the thin film. After analyzing data, we select 4 kV as our working voltage in our experiment to sputter our sample.

After a series of comparisons, the most optimized sputtering condition is selected as follow: a voltage of 4 kV, a current of 0.5 mA, and an incident angle of 30°.

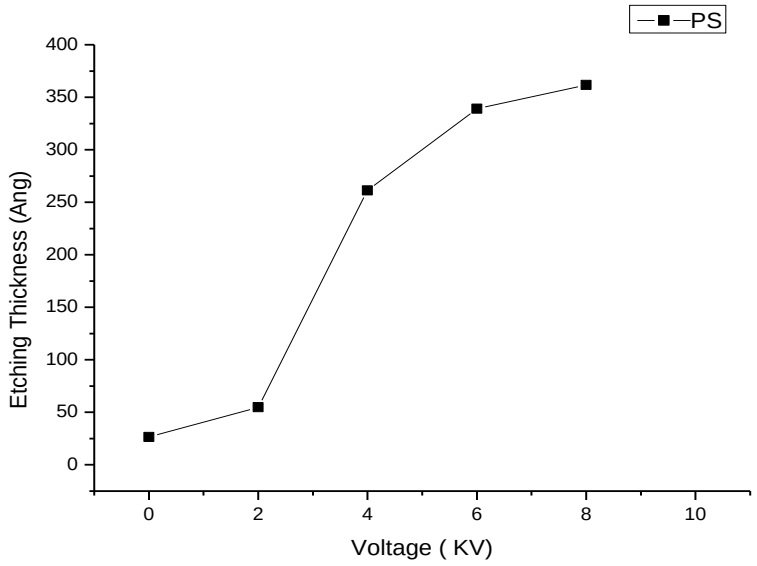


Figure4- 2 Sputtering rate as a function of voltage of an Ar ion beam

4.2 Sputtering rate for pure PS and PMMA thin film

In order to obtain high resolution pattern on PS/PMMA thin film, it is necessary to make the thickness variance large enough. The sputtering rate for pure PS and PMMA thin film under same condition is the basic for sputtering PS/PMMA blend film.

The PS thin films are prepared by PS solution with the concentration of 75 mg/ml, and the PMMA thin films are prepared by PMMA solution with the concentration of 70 mg/ml. The original thickness for PS thin film is around 4500 angstrom, while PMMA thin film is around 5000 angstrom. With higher original thickness, we can get more data to analyze. For PS thin film, we sputtered every 2 minutes to measure sputtered thickness. After 16 minutes, the PS thin film layer is sputtered out and only Si wafer substrate is left.

After collecting data, we use Original software to get figure 4-3, and fit data to get the two straight lines. The slope of each straight line individually represents the etching rate of both polymers, and can be calculated by the software as well. From it we can see the etching rate of PMMA, 736 Angstroms/min, which is significantly larger than that of PS, 283 Angstroms/min.

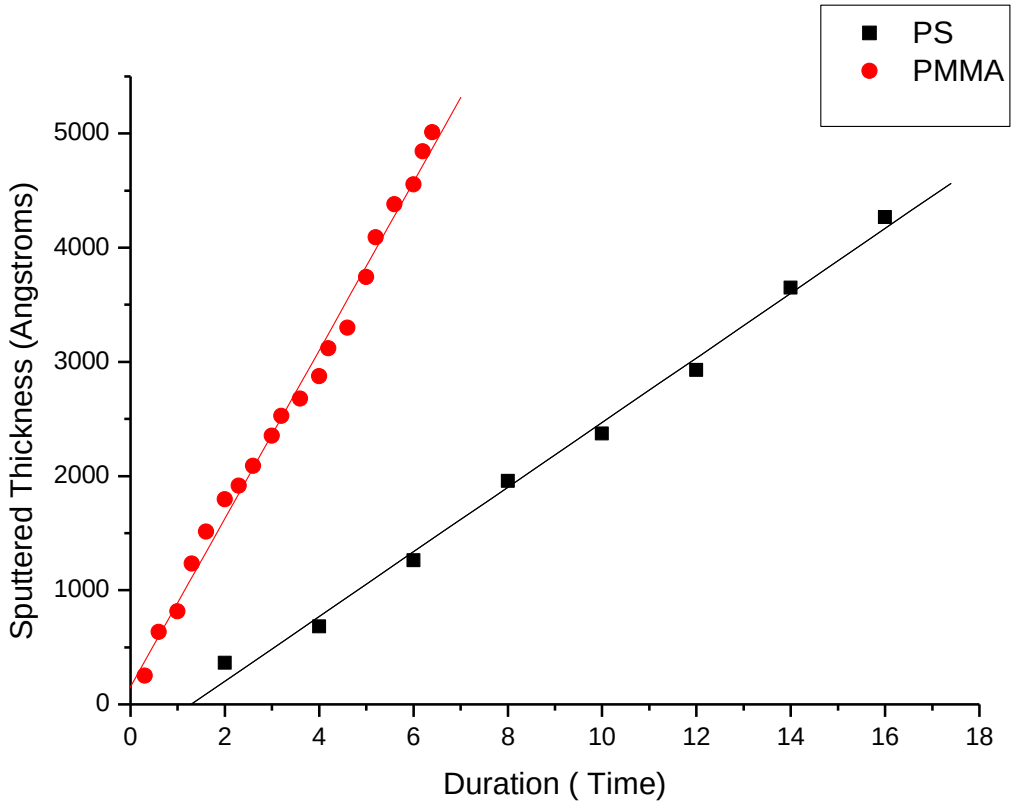


Figure4- 3 Comparison of thickness vs time for PMMA and PS films

4.3 Sputtered PS/PMMA blend thin film

According to our previous study on pure PS and PMMA, it is clear that PS and PMMA has different etching speed. Etching speed for PMMA is much faster than that of PS under same sputtering condition. In addition, in PS and PMMA thin film, phase segregation morphology can be easily obtained. Since big thickness difference is necessary to obtain high quality pattern, we have to select an appropriate sputter time for etching PS/PMMA polymer thin film. Based on the etching speed we obtained above, 5 minutes is chosen as sputter time. Therefore, after 5 minutes sputtering, PMMA will be etched around 736 angstroms/min × 5 minutes = 3689 angstroms. At

the same time, PS will be etched around 283 angstroms/min × 5 minutes = 1415 angstroms. Thus this obvious sputtered thickness difference will contribute to a higher resolution pattern.

In the following step, first, pattern on silicon wafer mad by blend polymer is analyzed. Then, patterns on titanium substrate are analyzed.

4.3.1 PS/PMMA spin cast on silicon wafer

To compare the morphology of different polymer blend ration, we have to spin cast different blend polymer onto the silicon wafer to get polymer thin film. The films were subsequently annealed at 180 °C in a vacuum oven for 12 hours to achieve chemically stable condition. After that, the phase segregation of the blend polymer thin film is achieved. Then we sputtered samples for 5 minutes to etch the polymer surface. Last, in order to leave nice pattern, residue polymer on the silicon wafer should be removed by putting into the high temperature heater. The temperature we used should be higher than the melting point of PS and PMMA but lower than that of silicon wafer. So we select 700 °C to remove polymer. After removing polymer, a good pattern is able to be created after following the procedures above.

The AFM images of spun cast blend thin film are show in row A of Figure 4-4. Column 1, 2, 3 corresponding to the blend compositions of weight ratio of 1:1, 1:3 and 3:1 PS to PMMA from left to right. Phase segregation can be easily found. The patterns are composed of either hole or island morphologies. In row D of Figure 4-4, we can compare the pattern quality of different polymer ration. For ratio of 1:1, in D1 of figure 4-4, only some non-uniform pattern is achieved. For ratio of 1:3, in D2, the uniform and regular pattern is achieved. For ratio of 3:1, no patter is obtained.

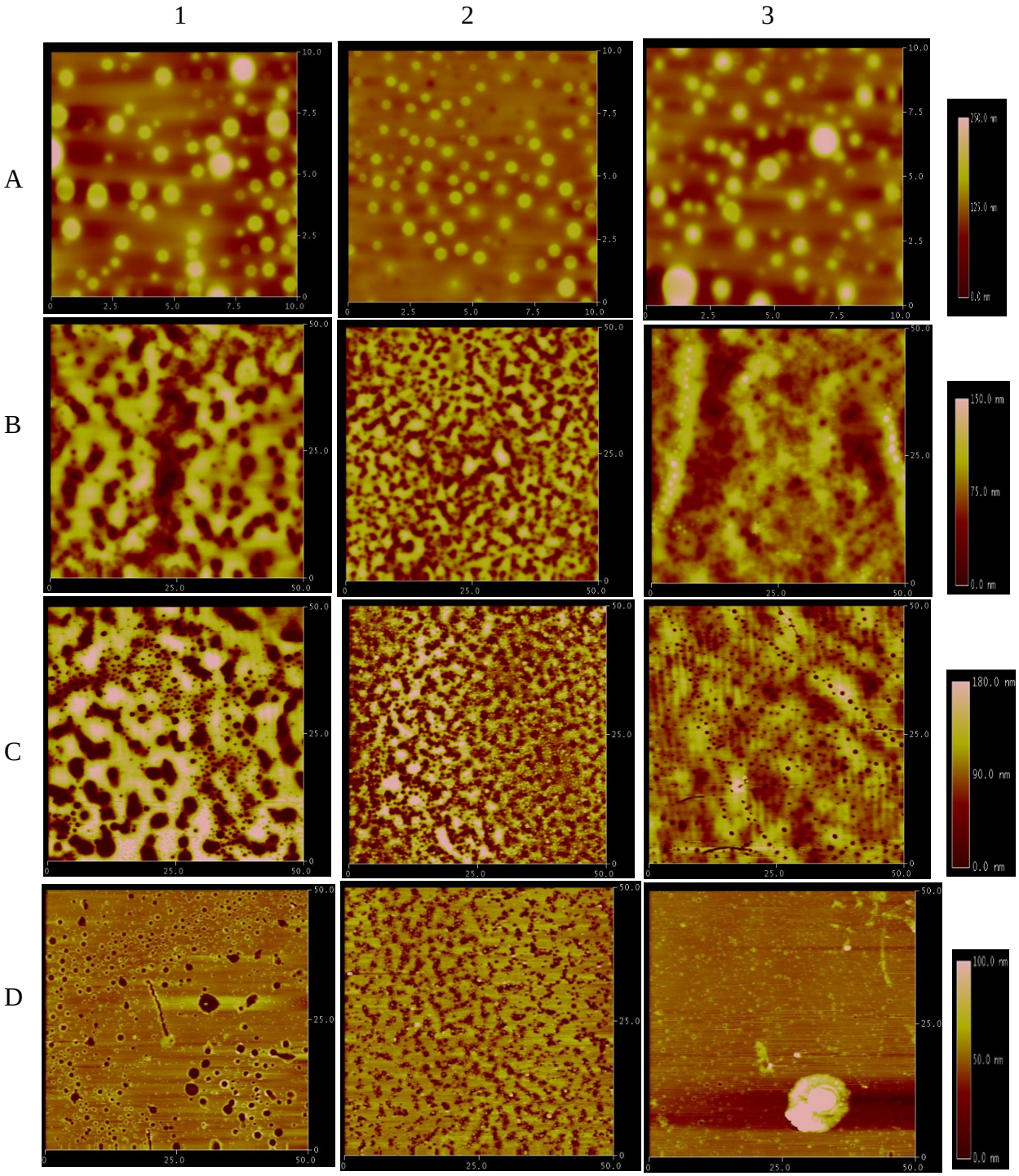


Figure4- 4 Row A (1-3): AFM topography scan of as-cast PS/PMMA on the silicon wafer. Row B(1-3): AFM topography scan of the films in row A after annealing 12 hours at 180 ℃ in a vacuum of 10^{-4} Torr. Row C (1-3): AFM topography scan of the films in Row B after 5 minutes Ar ion etching method described previously. Row D (1-3): AFM topography scan of films in Row C after 30 minutes in 700 ℃ high temperature heater to remove polymer

In order to understand what the hole or island represent in figure 4-4, analysis of both topographical and frictional image are necessary. Left image in row A of figure 4-5 illuminates that light color spots means high surfaces and dark ones means lower planes. However, in the frictional image, hard materials are showed in dark color, soft materials are showed in light color. So we can combine left image with right image, light dot in left image relate to the dark dot in right image. Normally, PS is harder than PMMA. So in left image, the light island represents PS, PS is higher than PMMA, and the etching speed of PS is less than PMMA, all this factors result in the pattern form on the surface of silicon wafer. In row D of figure 4-4, we can see 1:3 ration polymer thin films has best pattern. In order to evaluate the quality of these patterns better, we have to analyze the topographical image of three samples.

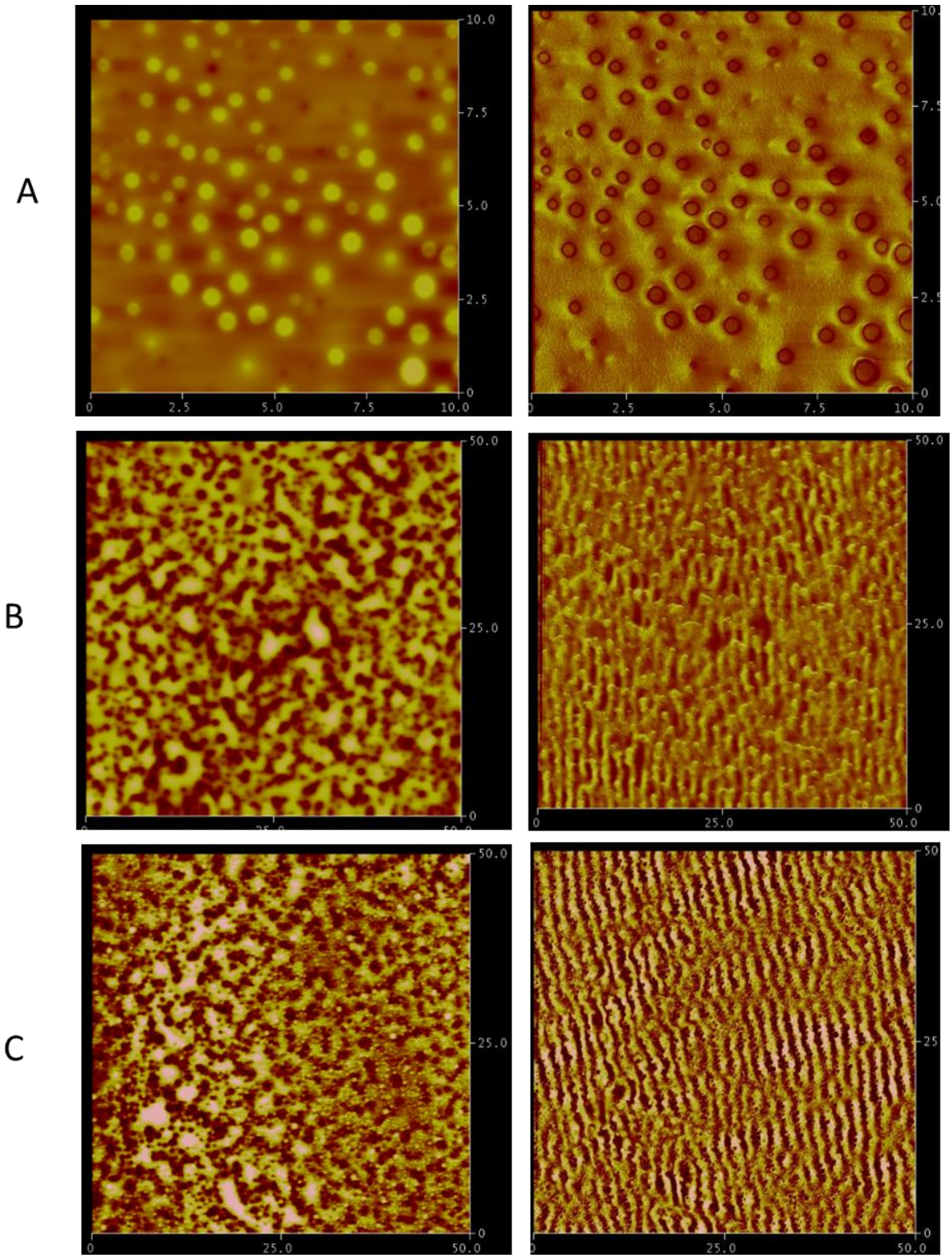
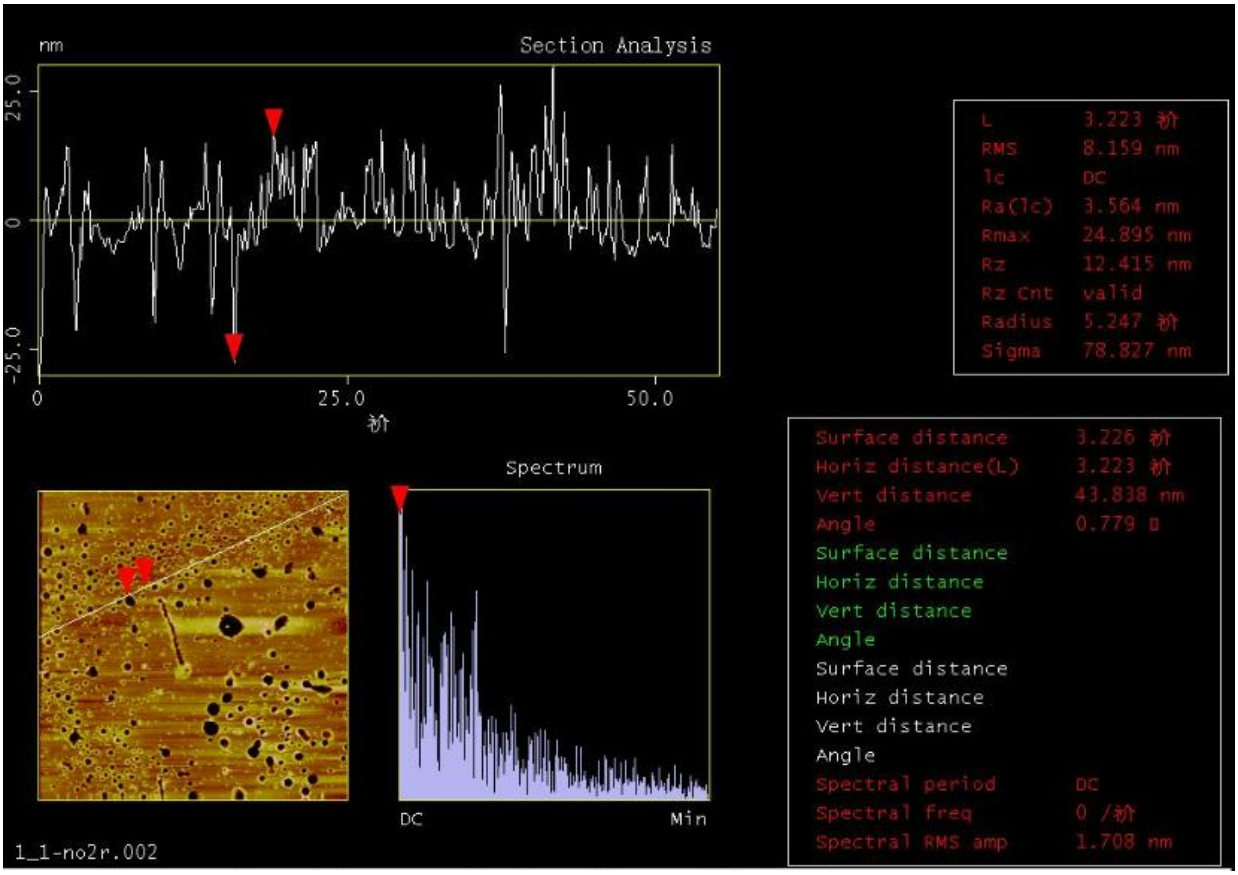
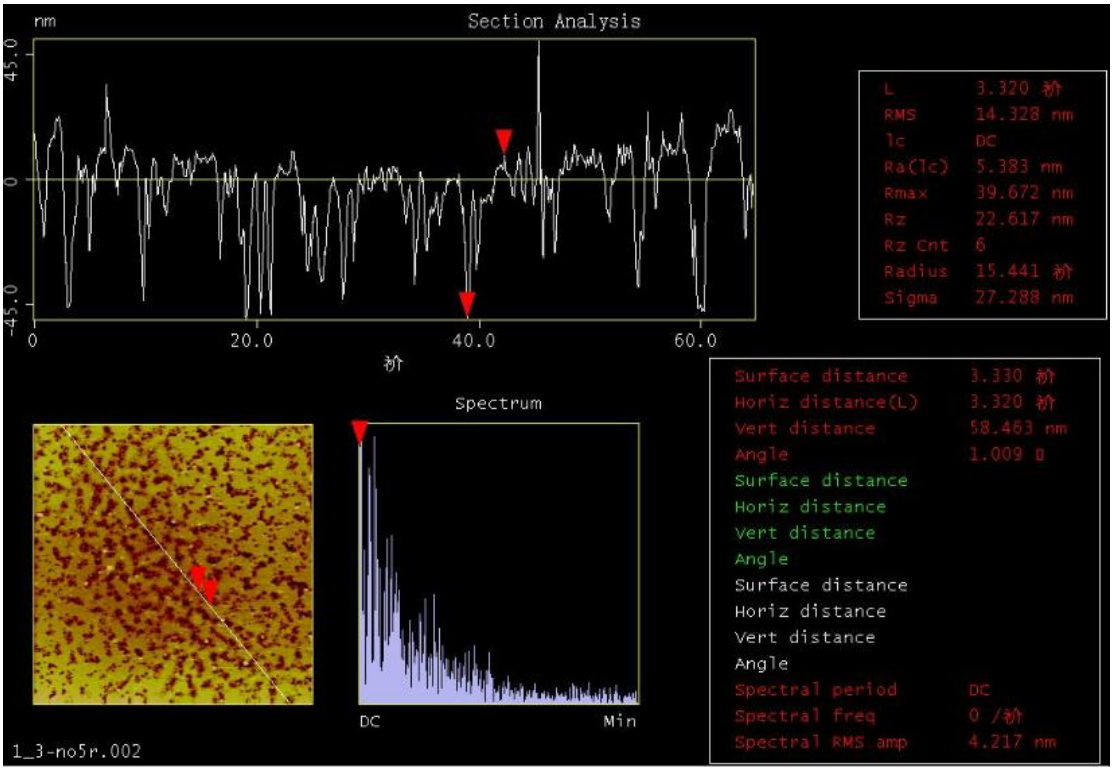


Figure4- 5 Topographical (left) and frictional (right) image of PS : PMMA = 1:3 films as spin-casting (A), after annealing for 12 hours at 180 °C (B), and after 5 minutes sputtering (c)

The images in Figure 4-6 are obtained by running section analysis, which the most representative domain is selected to analyze thickness change, in the software of NanoScope. We select most representative domain to analysis thickness change. By this way, the height change of the surface is easy to be observed. In image (A) of figure 4-6, we can see the average vertical distance of 1:1 thin film pattern is around 43nm. In image (B), the average vertical distance of 1:3 thin film pattern is around 58 nm, and the biggest vertical distance can even reach to 101nm. In image (C), the average vertical distance of 3:1 thin film pattern is just 7 nm, which means almost no pattern onto the thin film. Therefore, by comparison between 3 images, the 1:3 ratio of PS and PMMA polymer blend thin film has the highest quality pattern which can be used as a possible way for lithography.



(A)


nm
Section Analysis
45.0
0
-45.0
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20.0
40.0
60.0
L 3.320 μm
RMS 14.328 nm
lc DC
Ra(lc) 5.383 nm
Rmax 39.672 nm
Rz 22.617 nm
Rz Cnt 6
Radius 15.441 μm
Sigma 27.288 nm
Spectrum
DC
Min
Surface distance 3.330 μm
Horiz distance(L) 3.320 μm
Vert distance 58.463 nm
Angle 1.009 D
Surface distance
Horiz distance
Vert distance
Angle
Surface distance
Horiz distance
Vert distance
Angle
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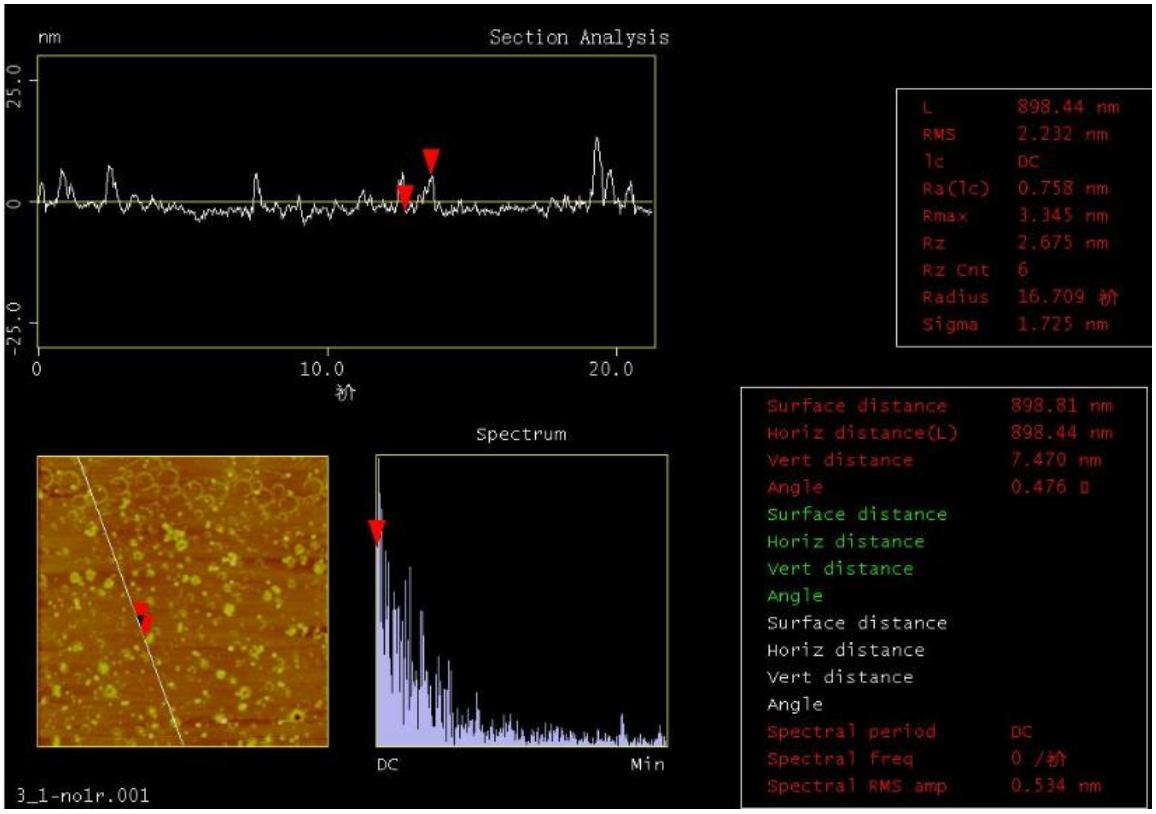
1_3-no5r.002

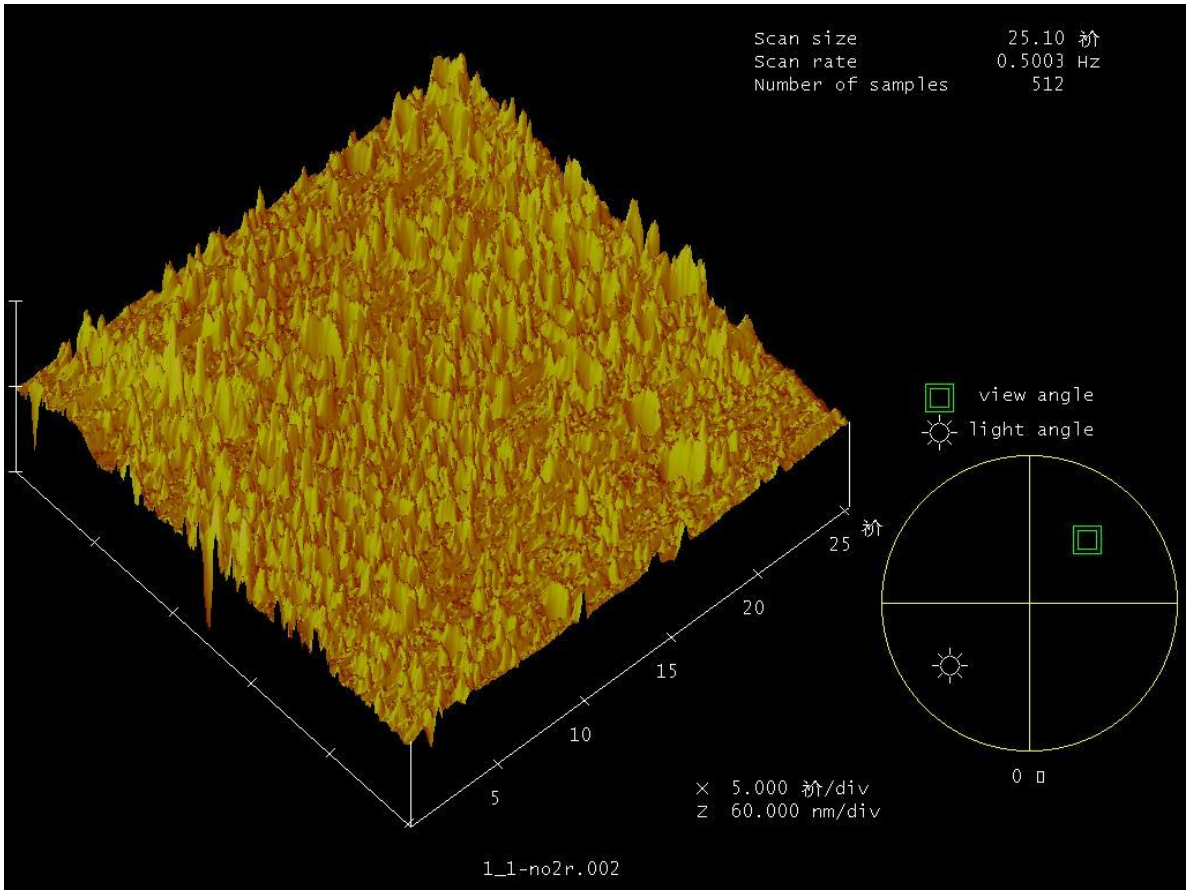
(B)



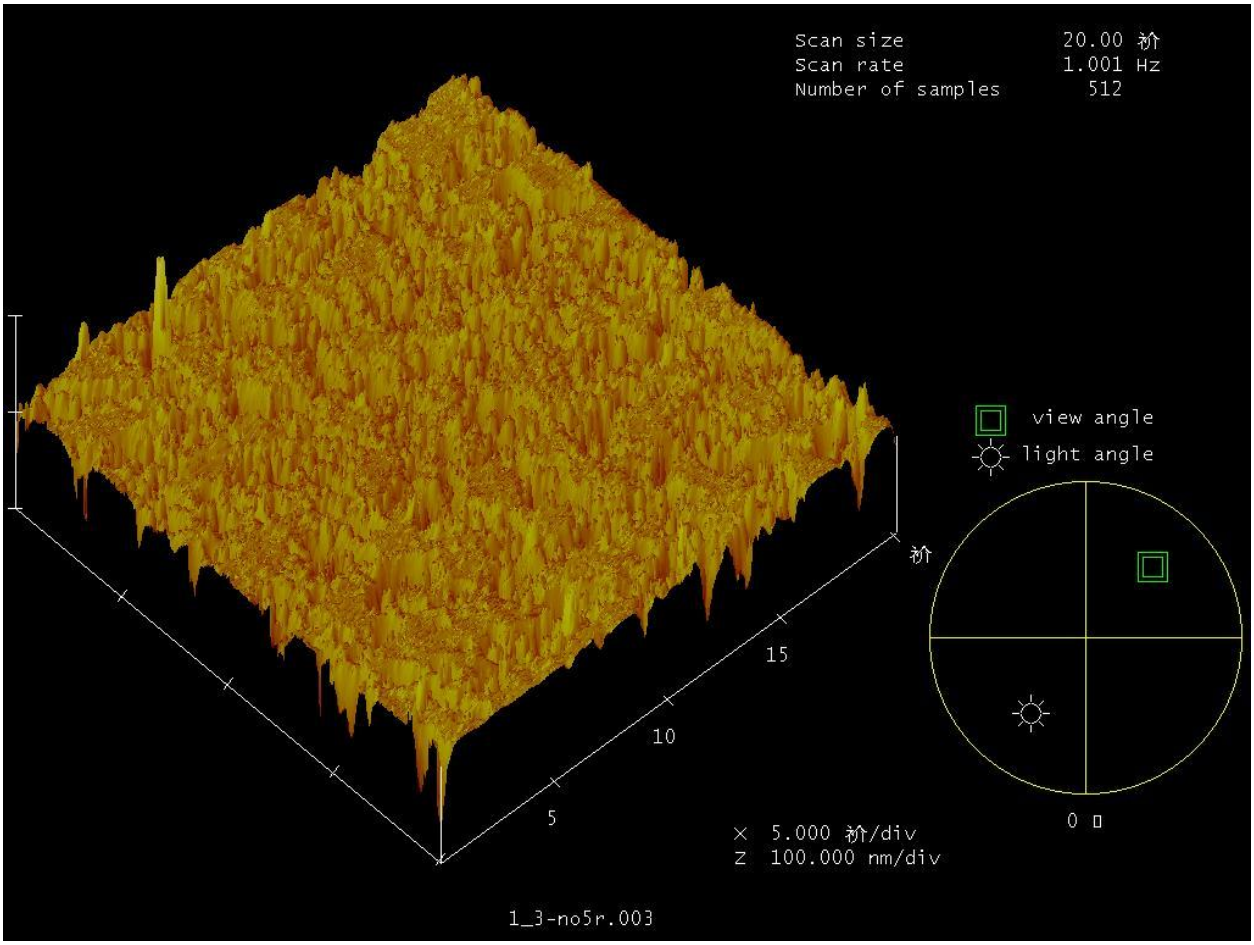
(C)

Figure4- 6 Section analysis by NanoScope software: (A) PS:PMMA=1:1, (B) PS:PMMA=1:3, (C) PS:PMMA = 3:1

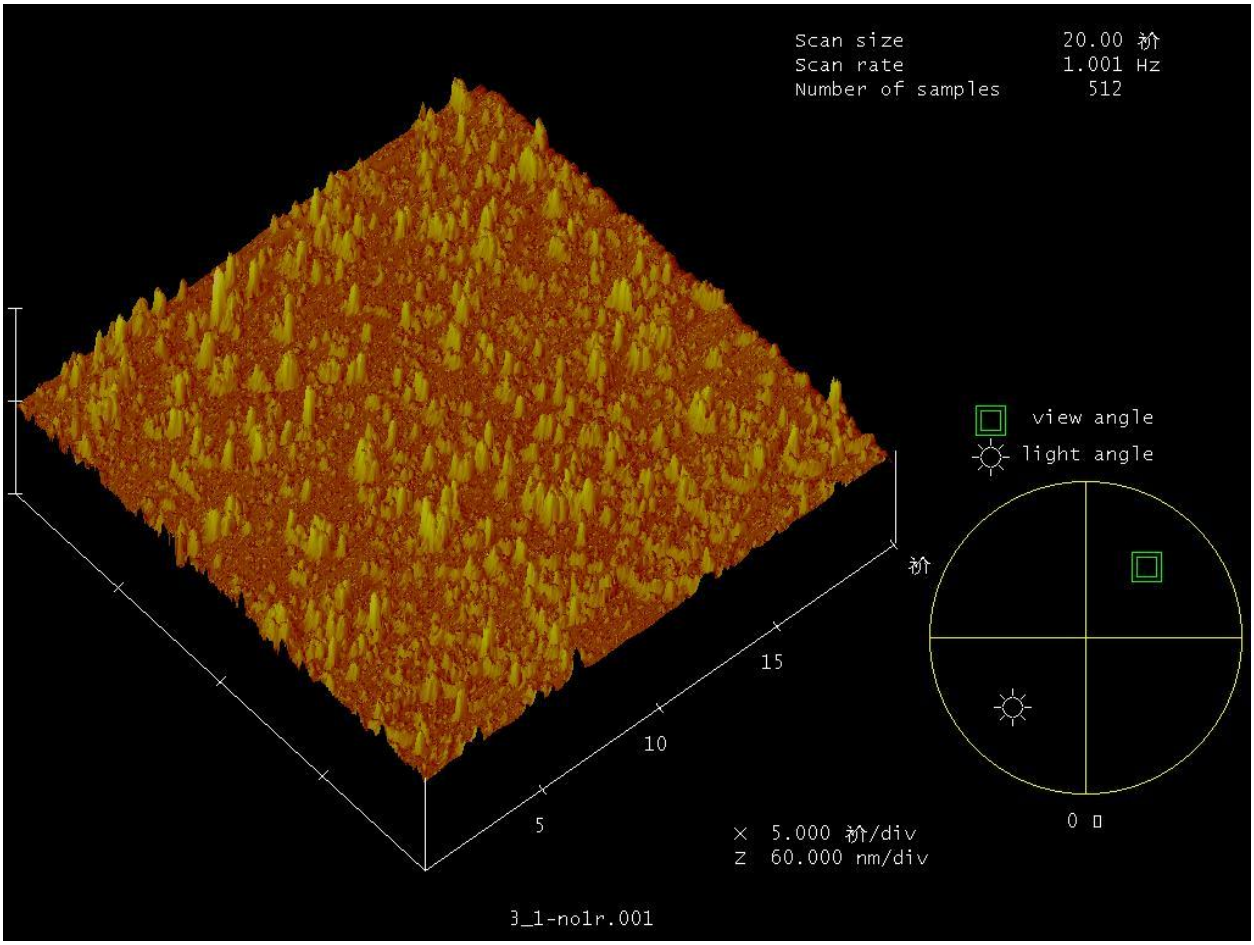
NanoScope software can also be utilized to analyze the morphology of the sample. In figure 4-7, more visualized image can be obtained by surface plot function in NanoScope. We can see the surface condition of 1:3, which shows in image (B) of figure 4-7, exhibit high resolution pattern. From the figure, we find that the sputtered sample has high resolution. On the other hand, for the 3:1 condition, which shows in image (C) of figure 4-7, there is no obvious height change on the surface. This result better proves our conclusion that 1:3 polymer blend thin film can create nice pattern on silicon wafer.


Scan size 25.10 μm
Scan rate 0.5003 Hz
Number of samples 512
view angle
light angle
5
10
15
20
25 μm
0 °
X 5.000 μm/div
Z 60.000 nm/div
1_1-no2r.002

(A) PS:PMMA = 1:1


Scan size 20.00 μm
Scan rate 1.001 Hz
Number of samples 512
view angle
light angle
μm
15
10
5
0 °
X 5.000 μm/div
Z 100.000 nm/div
1_3-no5r.003

(B) PS : PMMA = 1:3



(C) PS: PMMA = 3:1

Figure4- 7 Surface plot by NanoScope software. (A) PS:PMMA=1:1, (B) PS:PMMA=1:3, (C) PS:PMMA=3:1

4.3.2 PS/PMMA spin cast on Ti deposited surface

After successfully acquiring polymer patterns on the surface of silicon wafers, the spin casting and sputtering conditions are confirmed to be valid. These parameters will be imported to initiate a same control experiment which uses silicon wafer with a titanium deposited surface. The thickness of the titanium deposited onto the silicon surface is around 419 angstroms. In order to utilize this pattern onto titanium, we have to make sure the titanium layer cannot be sputtered out.

4.3.2.1 Sputter 3 minutes on Titanium thin film

Based on previous result about PS and PMMA etching rate, we first set 3 minutes as sputtering time to etch the sample. The same analyzing methods are still employed to be functional in this case.

The blend thin film surfaces on titanium are show in row A of Figure 4-8. Column 1, 2, 3 corresponding to the original blend compositions of weight ratio of 1:1, 1:3 and 3:1 PS to PMMA. In row D, after removing polymer, the pattern is presented. Like the pattern on the silicon wafer, for ratio of 1:1, in D1 of figure 4-4, only some non-uniform pattern is achieved. For ratio of 1:3, in D2, the uniform and regular pattern is achieved. For ratio of 3:1, we can hardly see pattern on the surface.

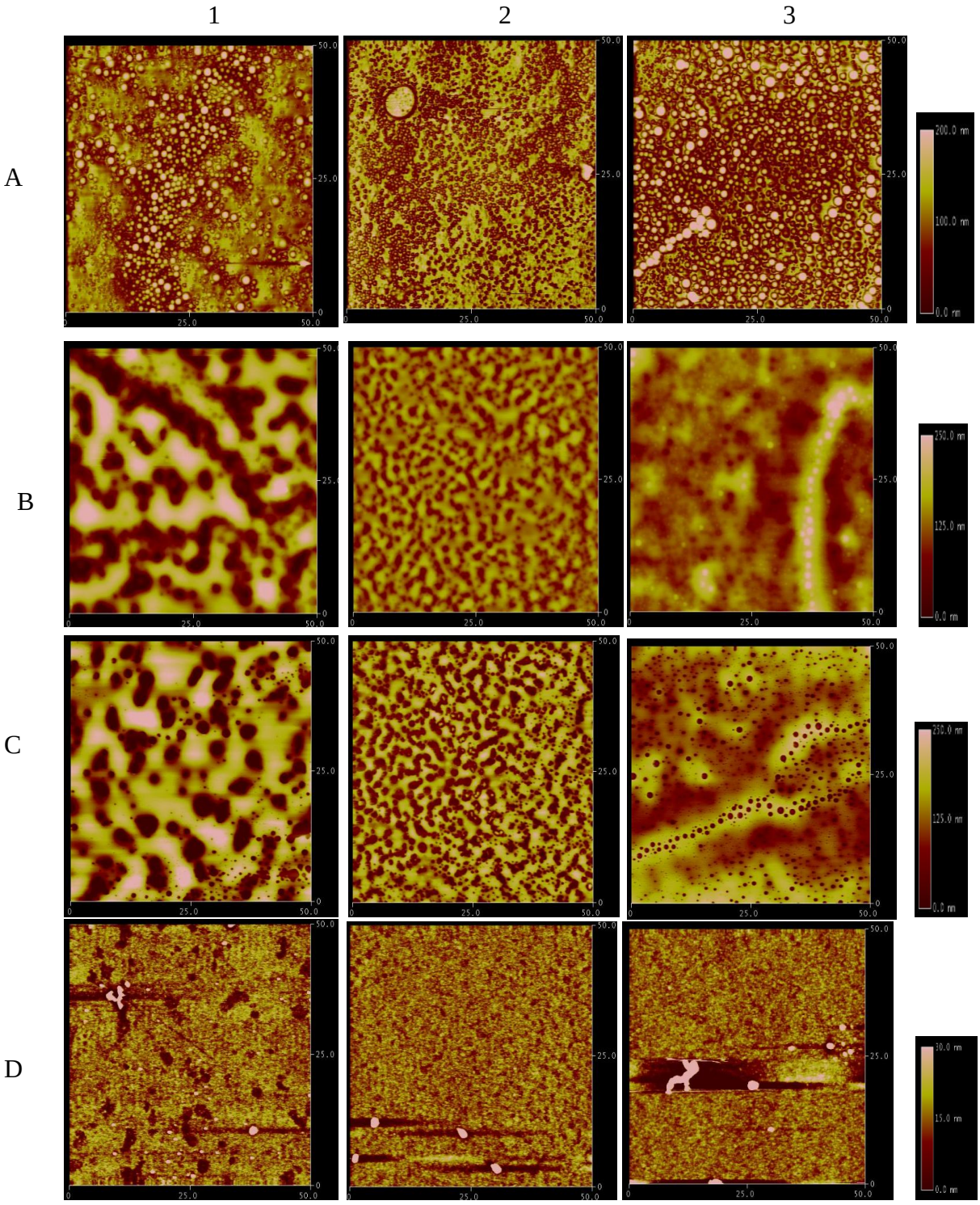
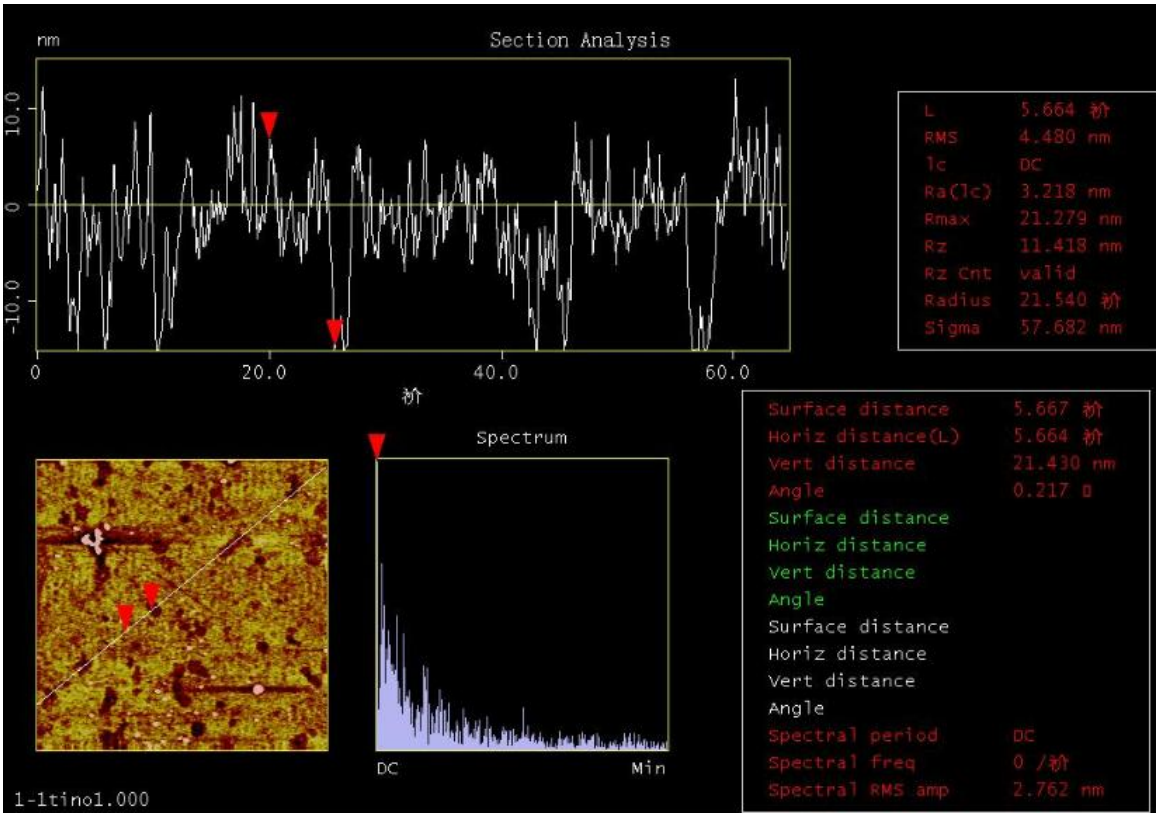
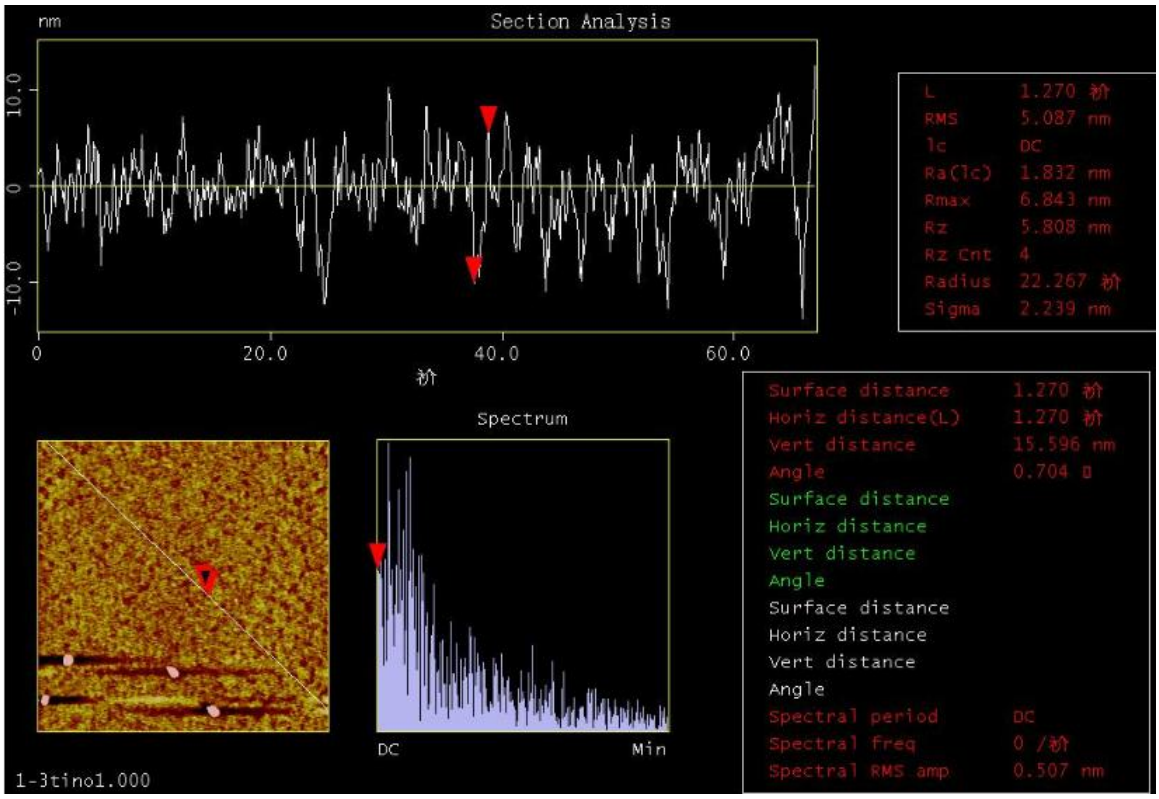


Figure4- 8 Row A (1-3): AFM topography scan of as-cast PS/PMMA on the Titanium layer. Row B(1-3): AFM topography scan of the films in row A after annealing 12 hours at 180 ℃ in a vacuum of 10^{-4} Torr. Row C (1-3): AFM topography scan of the films in Row B after 3 minutes Ar ion etching method described previously. Row D (1-3): AFM topography scan of films in Row C after 30 minutes in 700 ℃ high temperature heater to remove polymer

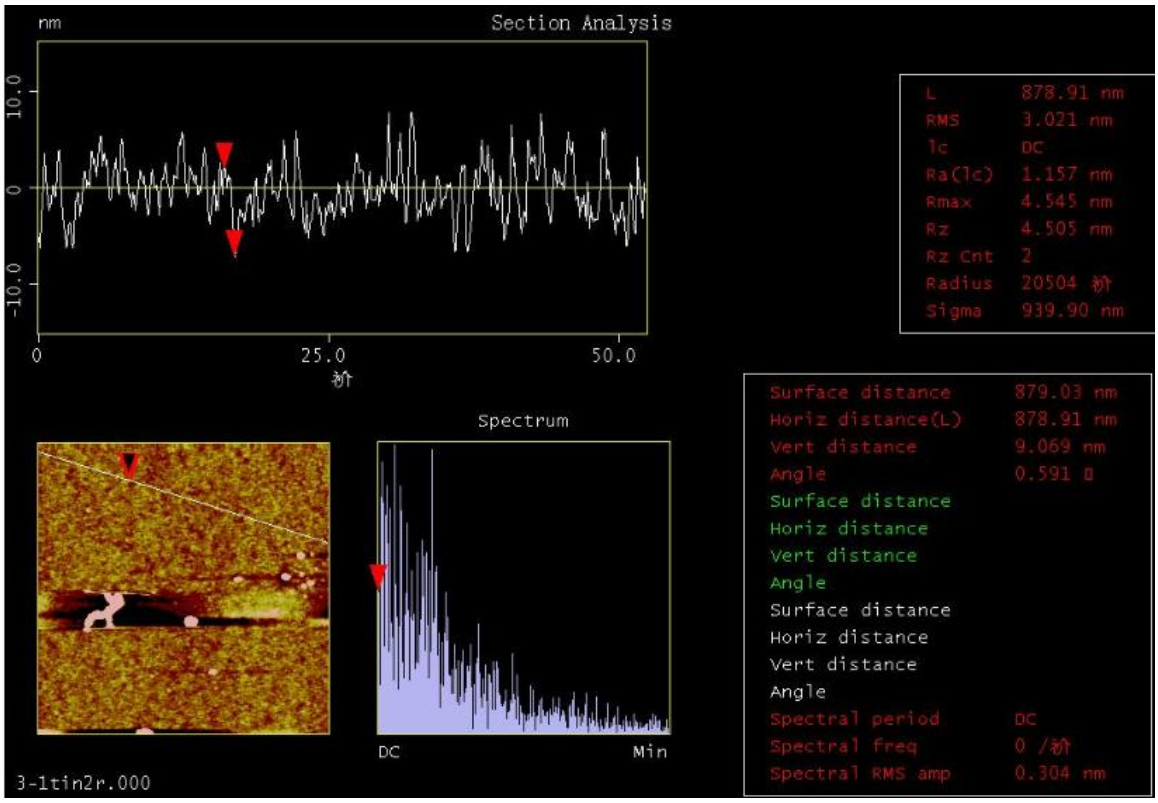
Figure 4-9 shows another set of images we obtained from the section analysis of NanoScope software. In image (A), we can see the average vertical distance of 1:1 thin film pattern is around 10 nm. In image (B), the average vertical distance of 1:3 thin film pattern is around 15 nm. In image (C), the average vertical distance of 3:1 thin film pattern is 9 nm. Therefore, almost no available pattern is found on the surface.



(A) PS:PMMA=1:1


nm
Section Analysis
10.0
0
-10.0
0
20.0
40.0
60.0
L 1.270 秒
RMS 5.087 nm
lc DC
Ra(lc) 1.832 nm
Rmax 6.843 nm
Rz 5.808 nm
Rz Cnt 4
Radius 22.267 秒
Sigma 2.239 nm
Surface distance 1.270 秒
Horiz distance(L) 1.270 秒
Vert distance 15.596 nm
Angle 0.704 D
Surface distance
Horiz distance
Vert distance
Angle
Surface distance
Horiz distance
Vert distance
Angle
Spectral period DC
Spectral freq 0 /秒
Spectral RMS amp 0.507 nm
Spectrum
DC
Min
1-3tino1.000

(B) PS : PMMA =1:3



(C) PS : PMMA = 3:1

Figure4- 9 Section analysis by NanoScope software on 3 minutes sputter for pattern on Titanium layer: (A) PS:PMMA=1:1, (B) PS:PMMA=1:3, (C) PS:PMMA = 3:1

In both scenarios, no visible patterns are available when PS/PMMA has a ratio of 3:1. Comparing all the conditions utilized in each experiment, a possible explanation is that sputtering time is not long enough to etch blend polymer thin film, so that there are no good

patterns formed. In order to complete nice pattern, the sputtering time should be raised reasonably.

4.3.2.2 Sputter 4 minutes on Titanium thin film

In order to get nice pattern on Titanium surface, increasing sputtering time is necessary. Considering a long time etching may damage the whole titanium layer, we select 4 minutes as sputtering time to continue attempt.

In row A of figure 4-10, we can see the morphology of the sample after 4 minutes sputtering. Compared with the images from row C in figure 4-8, we can notice the height difference of 4 minutes sputtered sample is bigger than that of 3 minutes sputtered sample, which means it is more possible to form a high resolution pattern with 4 minutes sputtering. Row B of figure 4-10 also shows a set of images of 4 minutes sputtered sample. In row B2, the pattern with 1:3 ratio can have a bigger height difference.

To better observe the height difference of the pattern, we use section analysis to observe the general pattern. In image B of figure 4-11, it is showed the average vertical distance on pattern for 1:3 ratio patterns is 40 nm, which is bigger than 14 nm, the average vertical distance of 3 minutes sputtered pattern. In the meanwhile, same phenomenon has also been found for1:1 and 3:1 ratio patterns. Both of their average vertical distance enhances to a certain extent, which means sputtering for 4 minutes is easier to obtain nice pattern than that for 3 minutes.

In figure 4-12, the morphology of pattern is more visualized. Image B demonstrates that the quality of pattern is very obvious. The height variation in this sample is visible in 1:3 ratio pattern.

In order to make sure we did not remove the titanium layer during this entire experiment, we need to know the sputtered thickness of our sample. From the section analysis, the vertical distance for the highest pattern is about 100nm, which is much smaller than the titanium we deposit on. Therefore, the titanium is not penetrated during the experiment.

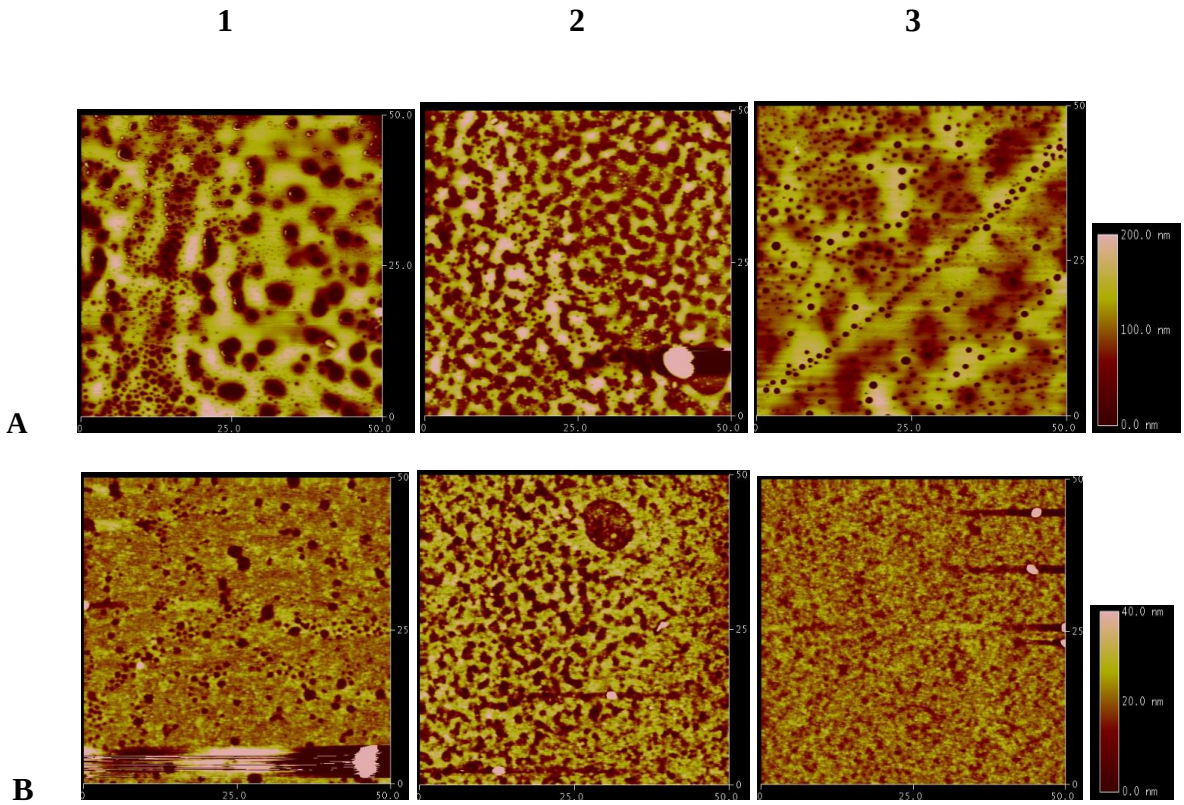
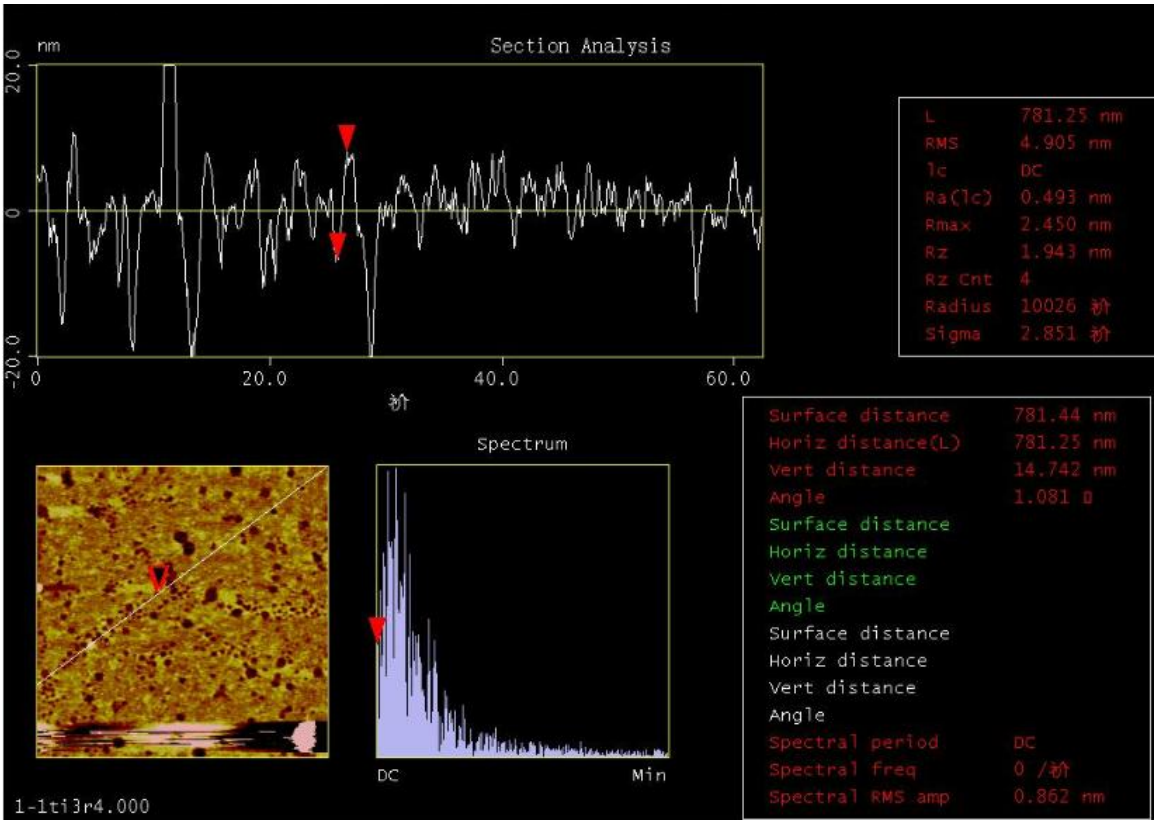
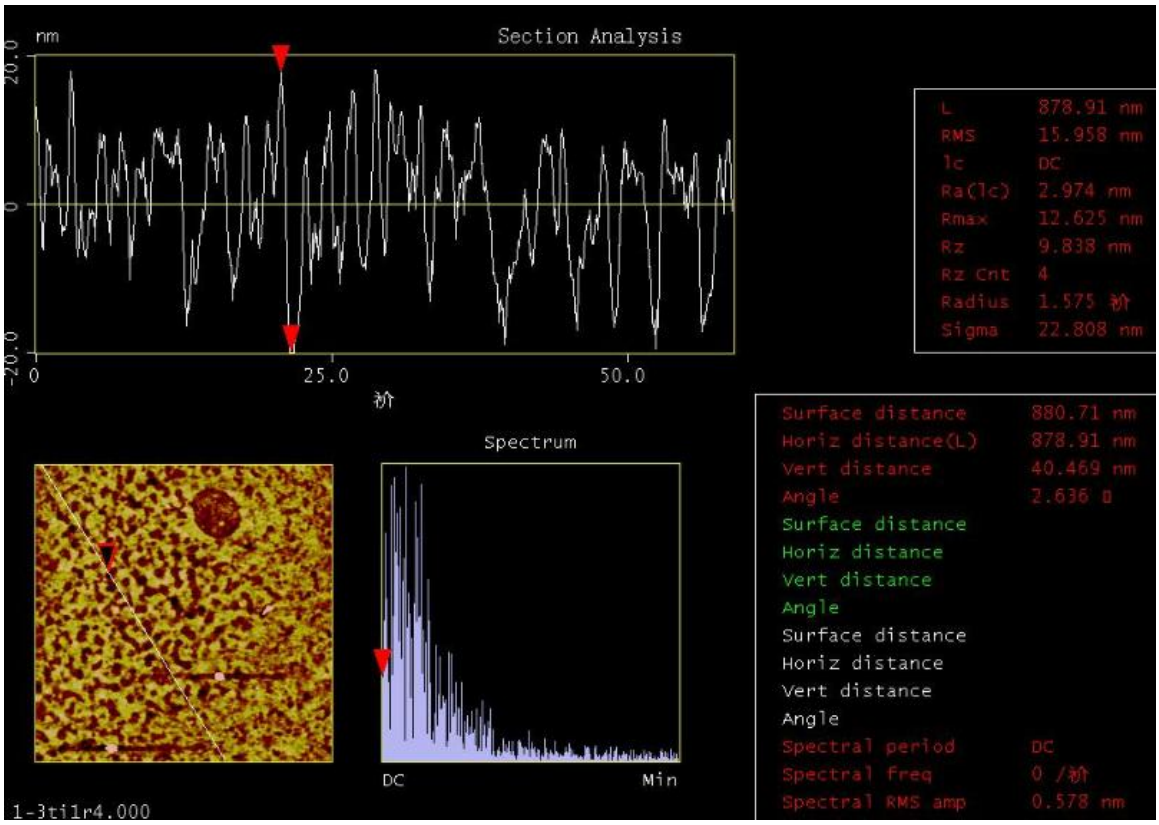


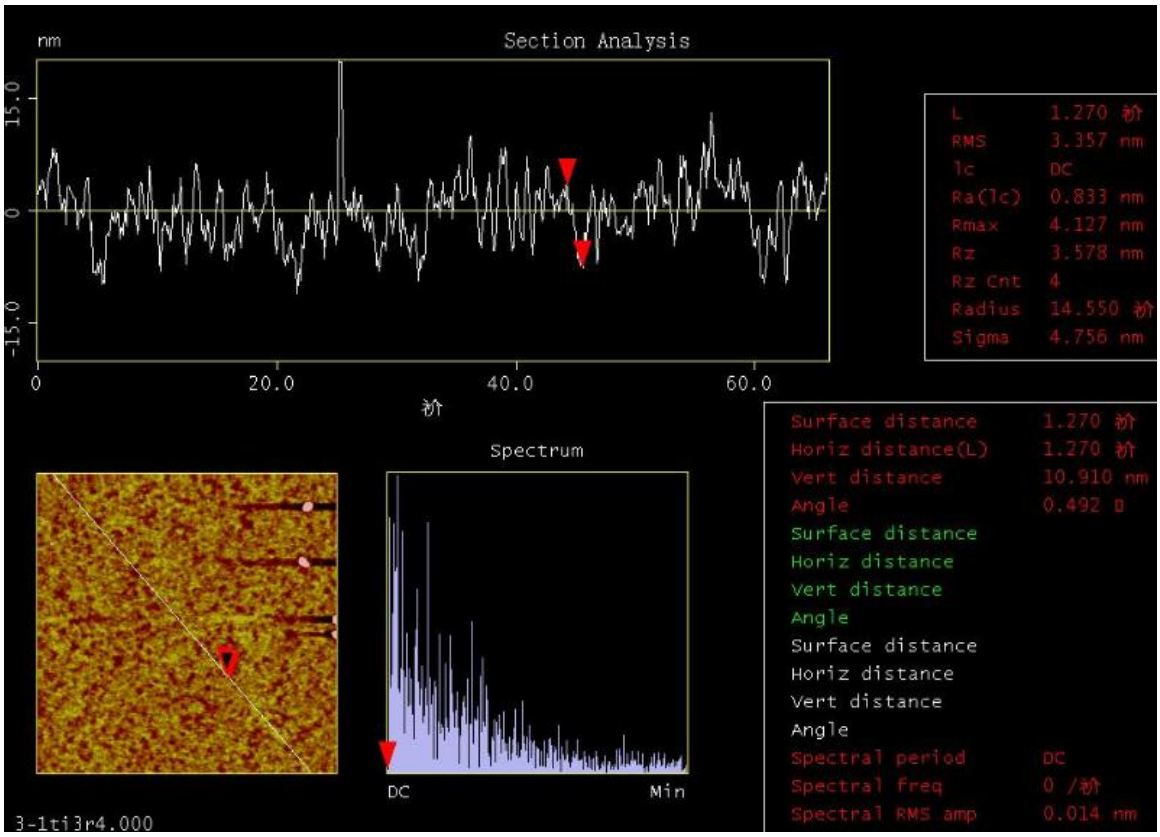
Figure4- 10 Row A (1-3): AFM topography scan of the films after 4 minutes Ar ion etching method described previously. Row B (1-3): AFM topography scan of films in Row B after 30 minutes in 700 ℃ high temperature heater to remove polymer


nm
Section Analysis
20.0
0
-20.0
0
20.0
40.0
60.0
L 781.25 nm
RMS 4.905 nm
lc DC
Ra(lc) 0.493 nm
Rmax 2.450 nm
Rz 1.943 nm
Rz Cnt 4
Radius 10026 nm
Sigma 2.851 nm
Spectrum
DC
Min
Surface distance 781.44 nm
Horiz distance(L) 781.25 nm
Vert distance 14.742 nm
Angle 1.081 D
Surface distance
Horiz distance
Vert distance
Angle
Surface distance
Horiz distance
Vert distance
Angle
Spectral period DC
Spectral freq 0 /nm
Spectral RMS amp 0.862 nm
1-1ti3r4.000

(A)

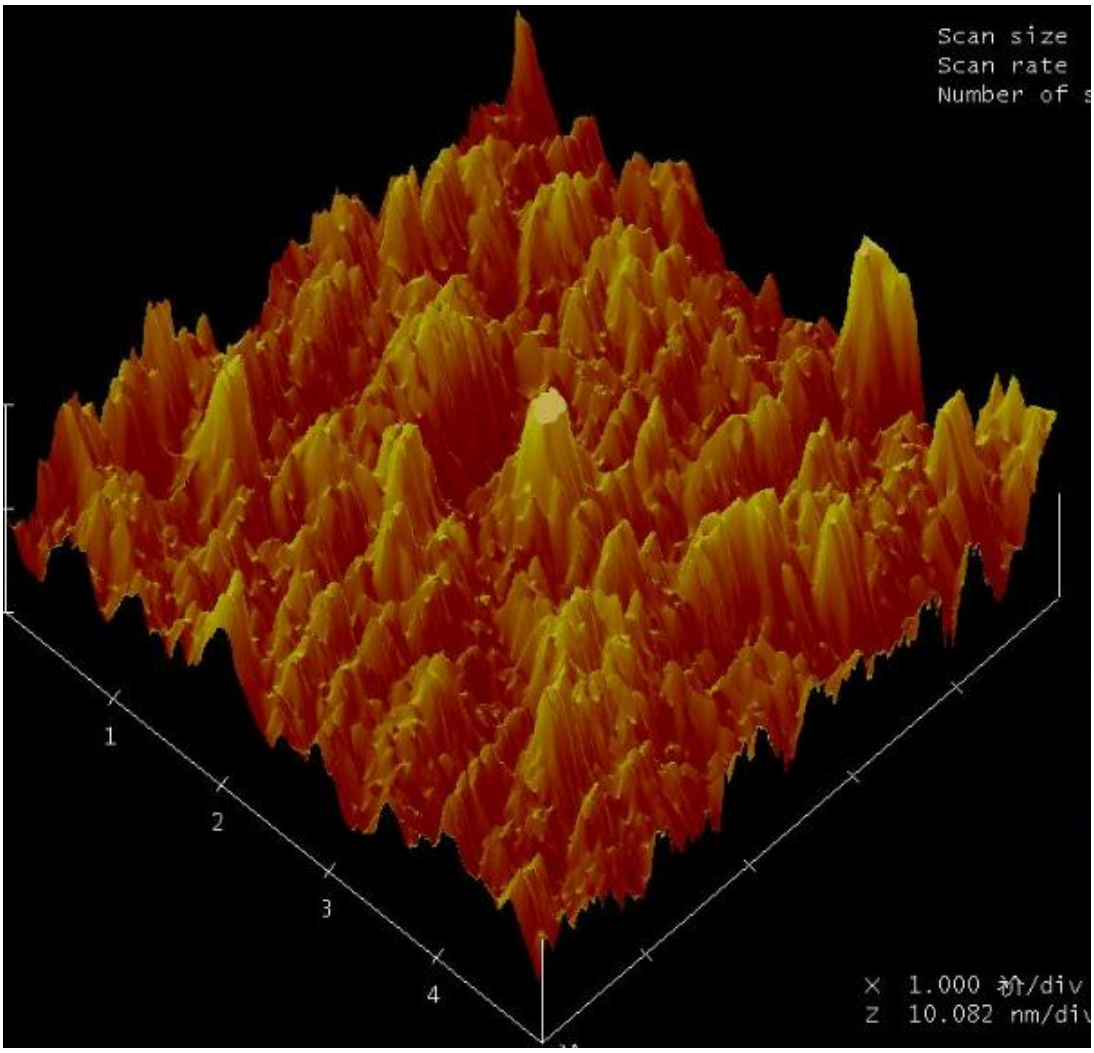

nm
Section Analysis
20.0
0
-20.0
0
25.0
50.0
L 878.91 nm
RMS 15.958 nm
lc DC
Ra(lc) 2.974 nm
Rmax 12.625 nm
Rz 9.838 nm
Rz Cnt 4
Radius 1.575
Sigma 22.808 nm
Spectrum
DC
Min
Surface distance 880.71 nm
Horiz distance(L) 878.91 nm
Vert distance 40.469 nm
Angle 2.636
Surface distance
Horiz distance
Vert distance
Angle
Surface distance
Horiz distance
Vert distance
Angle
Spectral period DC
Spectral freq 0 /
Spectral RMS amp 0.578 nm
1-3ti1r4.000

(B)

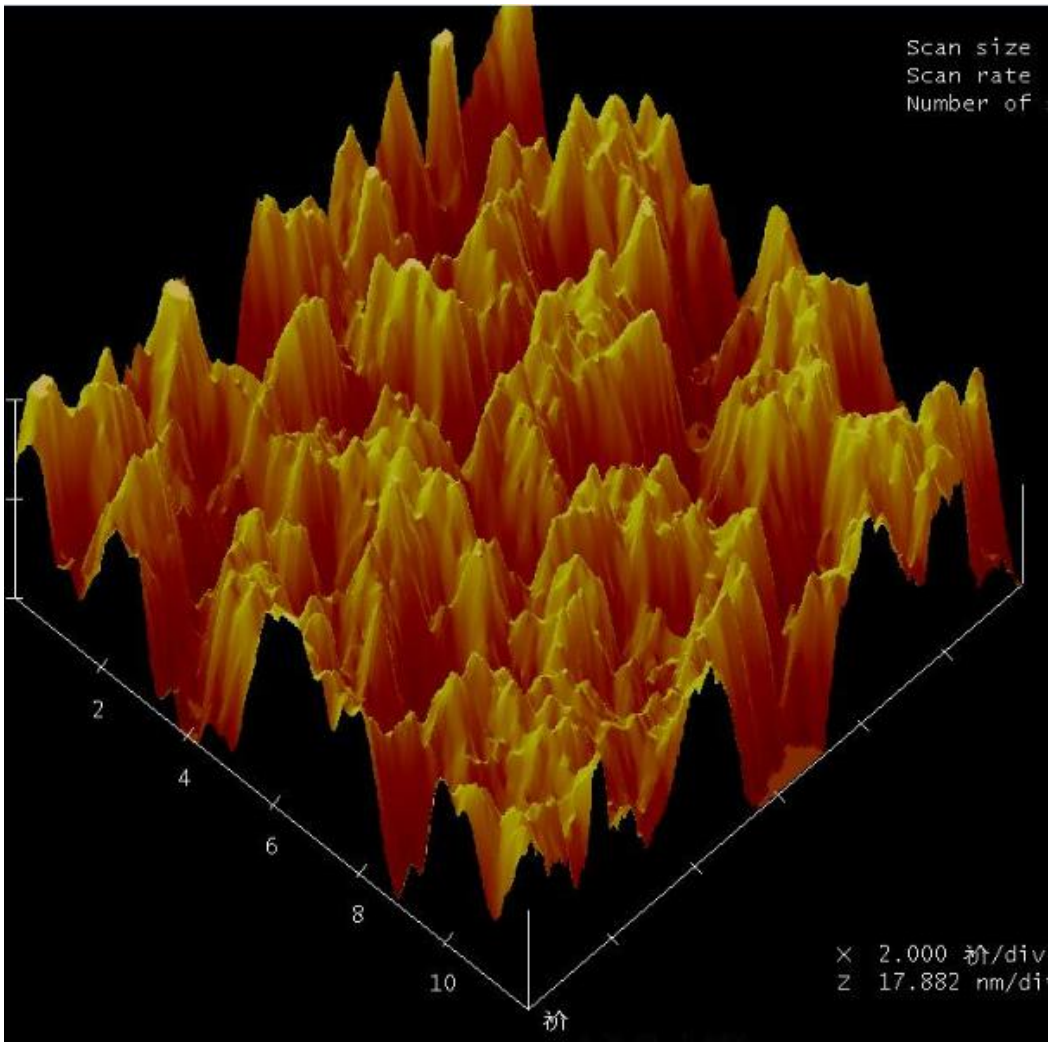


(C)

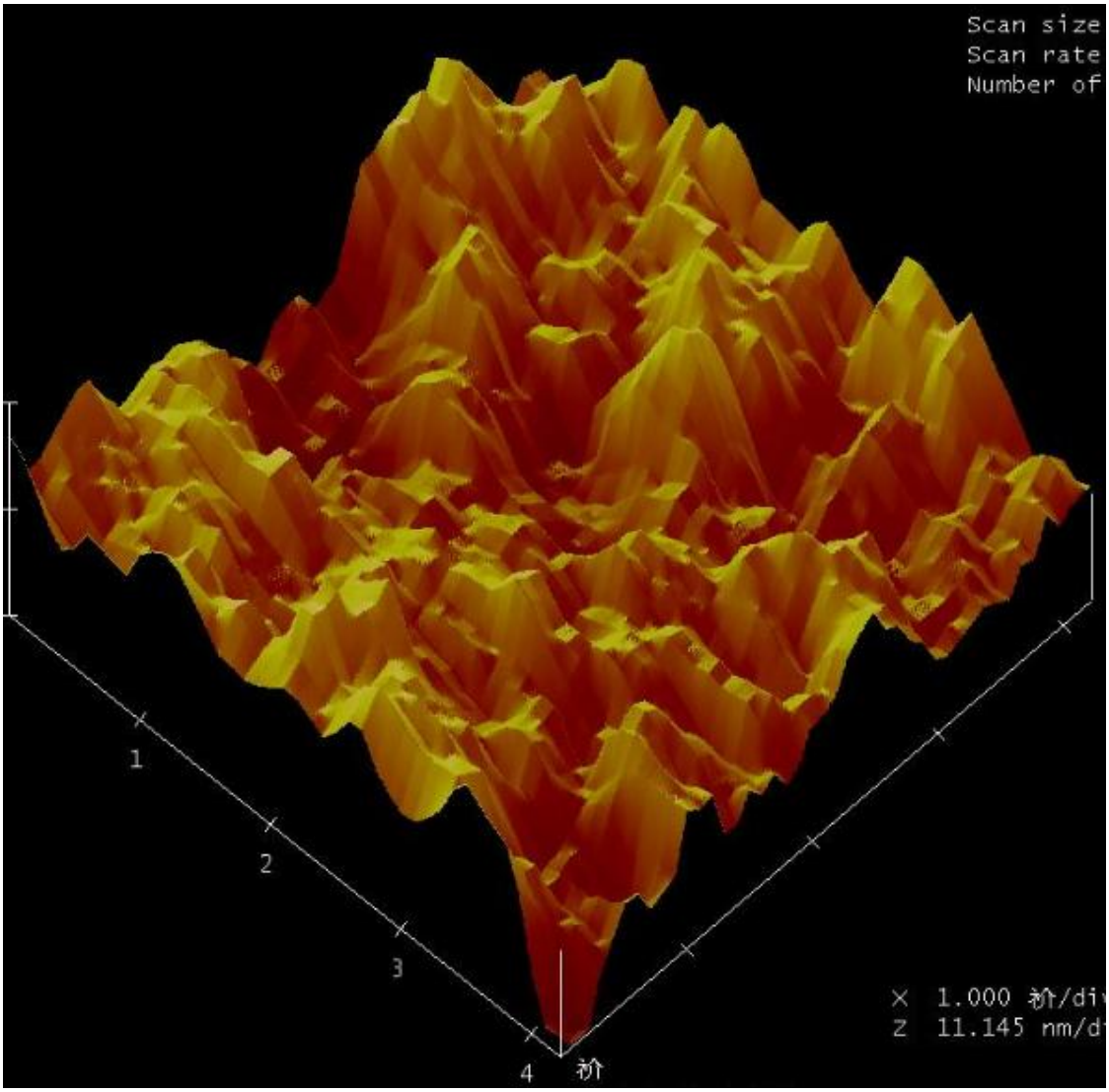
Figure4- 11 Section analysis by NanoScope software on 4 minutes sputter for pattern on Titanium layer: (A) PS:PMMA=1:1, (B) PS:PMMA=1:3, (C) PS:PMMA = 3:1



(A)


Scan size
Scan rate
Number of
2
4
6
8
10
X 2.000 μm/div
Z 17.882 nm/di

(B)



(C)

Figure4- 12 Surface plot by NanoScope software. (A) PS: PMMA=1:1, (B) PS: PMMA=1:3, (C) PS: PMMA=3:1

Chapter 5 Conclusion

The primary contributions of this work are introducing a new technical way to fabricate high resolution pattern on the titanium substrate.

The proposed technique is inspired by the existing nanolithography technical. Moreover, since the distinct morphological property of block polymer, PS/PMMA blend thin film is selected as our material. According to compare the quality of different composition ratio of blend polymer thin film, the composition ratio of 1:3 blend thin film have best pattern, which means the resolution of the pattern is very high. With the analysis by AFM, high quality pattern has been achieved on the titanium substrate.

In conclusion, using block polymer to do lithography is a promising approach to produce high quality pattern.

Chapter 6 Future Work

In this project, we already tried 3 different ratio of PS/PMMA blend solution. In order to obtain better quality pattern, more phase segregation is necessary. By varying the experiment condition, such as concentration, annealing time, annealing temperature, speed of spin cast, and solvent, different phase segregation can be obtained. So there are a lot of things for us to change in order to achieve more phase segregation polymer thin film.

On the other hand, etching time is also an important parameter for us to achieve high resolution pattern. So we can increase etching time to obtain better pattern. Moreover, we also want to penetrate titanium layer to get titanium mixed with silicon pattern in order to apply to bio-tissue engineering.

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