Investigation of diblock copolymer morphology via solvent vapor annealing

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Abstract

The morphology of block copolymer, polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA) 66-b-67, is investigated with atomic force microscope(AFM) . The process to improve the morphology of the block copolymer uses selective solvents for solvent vapor annealing (SVA). The Hansen solubility parameters define the affinity of the solvent for the polymer templates. Acetone was found as a selective solvent for PMMA and less selective for PS. The appropriate lateral lamellar structure is determined for a solution with concentration of 12 mg/ml, annealed for 2.5 hours.

Contents

1 Introduction

A copolymer is a polymer derived from two or more monomeric species, as opposed to a homopolymer where only one monomer is used. A special kind of copolymer is called a "block copolymer". Block copolymers are made up of blocks of different polymerized monomers. PS-b-PMMA is short for polystyrene-b-poly(methyl methacrylate) and is made by first polymerizing styrene, and then subsequently polymerizing MMA from the reactive end of the polystyrene chains. This block copolymer is a diblock copolymer as it has two distinct blocks. The nanoscale structures created from block copolymers could potentially be used for creating devices for use in computer memory, nanoscale-templating and nanoscale separations. Block copolymers are interesting because they can "microphase separate" to form periodic nanostructures. Because the blocks are covalently bonded to each other, they can not demix macroscopically. Depending on the relative lengths of each block, several morphologies can be obtained.

2 Theory

In this study polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA) is used with block ratio 66/67. The PMMA has a CO double bond, which makes the polymer polar. The substrate for PS-b-PMMA is a silicon wafer. It is energetically more favourable for PMMA to move to the substrate, due to dipole-dipole interactions between the partial negative charges. Non-polar PS moves to the air interface.

2.1 AFM

Atomic force microscopy (AFM) is the most commonly used setup to investigate the morphology of block copolymers, because it is non-destructive. AFM, in tapping mode, produces phase images by oscillating a sharp tip attached to a cantilever above the sample. The oscillation frequency is altered by the presence of various features, hence building up an image of the morphology. However, there is a disadvantage of this method it can be dependent on the parameters of the image. It does not take the whole sample into consideration, but only a small section.

The phase and height images were recorded using the AFM in this study.

2.3 Solvent Vapor Annealing

The solvent vapor annealing swells the polymer film and increases the film thickness. Due to the interaction of the solvent with the polymers, the blocks are mobalized and can form other structures. The process is a time depending method, where the blocks are rearrangeing to a final structure at the energy minumum. This is describes by the flory-huggins parameter. It describes the interaction energies between the blocks and with the interfaces (air to polymer and polymer to substrate). The stability and sturcture is depending on the molecular weight and volume fraction of the two blocks. In this work we used symmetric block copolymers with the same molecular weight to fabricate lamellar structures on the surface.

3 Method

3.1 Preparation

Silicon wafers were prepared via placement in an ultrasonic bath, containing acetone, for 30 min. After this time, the wafers were thoroughly cleaned with flows of acetone, isopropanol and distilled water sequentially and dried using N_2 gas. This process was of high importance in order for the surface of the substrate to be clear of impurities and dust for optimal coating and to prepare the right polarity of the substrate for the block copolymer thin film.

The solution was prepared by accurately weighing 36mg of the polymer PS-b-PMMA 66/67, and combining it with 3.0ml of toluene. The solution was mixed on a vibrating stage, moving at around 800 RPM for 12h. Spin-coating was used to deposite a thin polymer film on the silicon substrate. The paramters which were used are the rotation speed of 4000 RPM, ramp 9 and time 30s.

Centripetal acceleration during spin coating causes the solution to spread across the wafer.

3.2 Analysis

Measurements of thickness, RMS roughness and domain period could be obtained using AFM measurements. Thickness measurements were determined by making a scratch on the surface of the sample. The scratch moved away the polymer top surface, and a simple scan crossing both the scratched and unscratched area enabled a thickness measurement to be calculated.

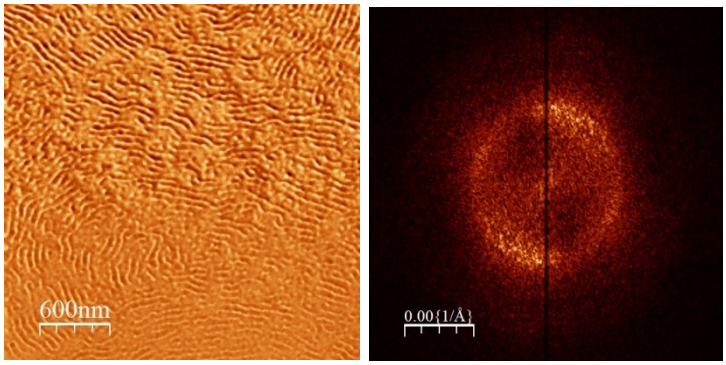
3.3 Solvent Vapor Annealing

The solvent vapor annealing process was used to order the polymers. The samples were placed in a glass container on a platform. The container was partially filled with acetone to a level half way below the platform. This was chosen as an acceptable volume as there was solvent left at the end of the annealing period. The solvent annealing process occurs in a closed container, the vapour pressure reaches thermodynamic equilibrium with the liquid phase. During this process, acetone was used as the solvent because it is known to make the PMMA within the BCP mobile.The samples were taken out, the colours observed on the wafers are caused due to interferece of the solvent vapours, a homogeneous colour across the sample indicates a constant thickness.

4 Results & Discussion

During the experiments with different time of solvent annealing between 1.5 and 3 hours with the time step, it was found the most appropriate time for annealing with acetone was 2.5 hours Fig. 1. This time of solvent annealing is the most suitable to obtain the lateral lamellar structure for this symmetric copolymer.

(a)



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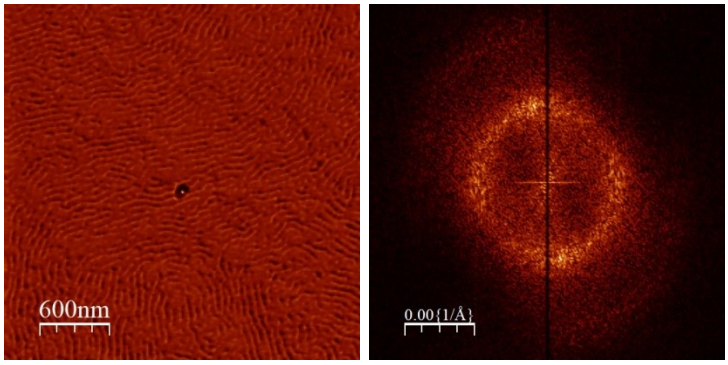

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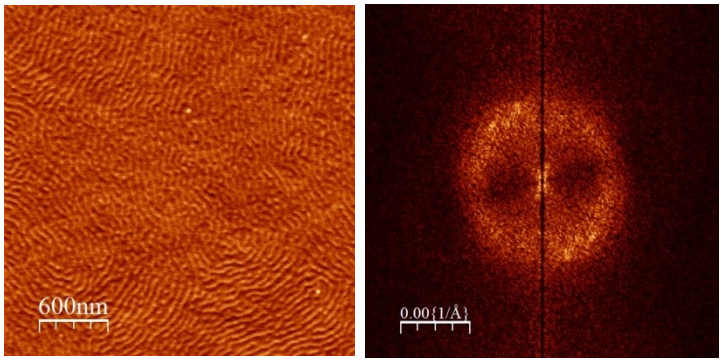

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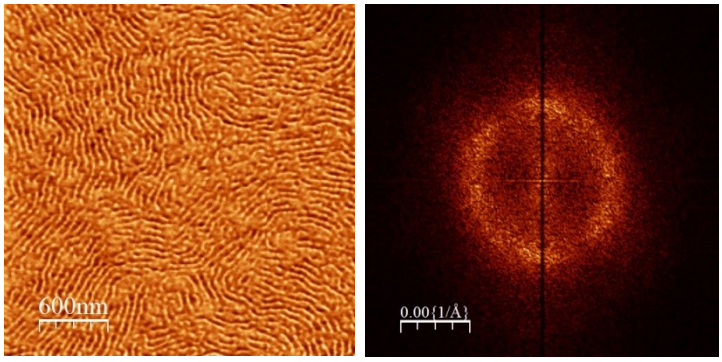

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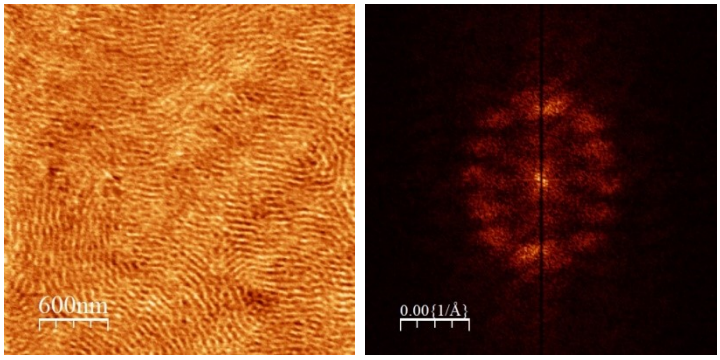


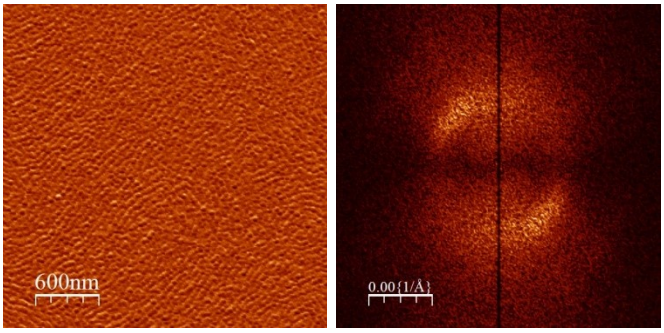
Figure 1: The morphology of samples after solvent vapor annealing with acetone and corresponding images of FFT analysis: (a) time of annealing 1h 50 min; (b) time of annealing 2h; (c) time of annealing 2h 10 min; (d) time of annealing 2h 20 min; (e) time of annealing 2h 30 min

After the solvent annealing with acetone the morphology of samples was checked with AFM. It was noted from literature that optimal results were found when the domain period of the sample matches the thickness. From analysis of the AFM images, the domain period was found to be 57 nm. From thickness measurements, it appeared to coincide with a concentration 12 mg/ml.

After annealing with acetone the samples were sputtered with 2 nm of silver, first sample without heating and then the others were sputtered and then heated to temperatures 100 °C, 150 °C, 170 °C respectively . The resulting morphology was checked with AFM. By comparison of the AFM phase images in this section, it can be noted that the morphology of the solvent annealed samples show better order after the plasma treatment with 5 times, which means that the sample was treated with a plasma pen and the whole sample was plasma cleaned 5 times, than the same procedure was made with 2 times of plasma cleaning. The sample which was heated to 100 °C has less pronounced order in lamellar structure than the samples which were heated to 150 °C Fig. 2. Two samples after solvent annealing with acetone were treated with plasma pen 2

times and 5 times respectively Fig. 3. This can also be observed from the FFT of samples, The FFT shows a slight elongation along the vertical axis - but no distinct directionality. After solvent annealing and sputtering with temperature of 150 °C the FFT follows a more precise ring structure.

(a)



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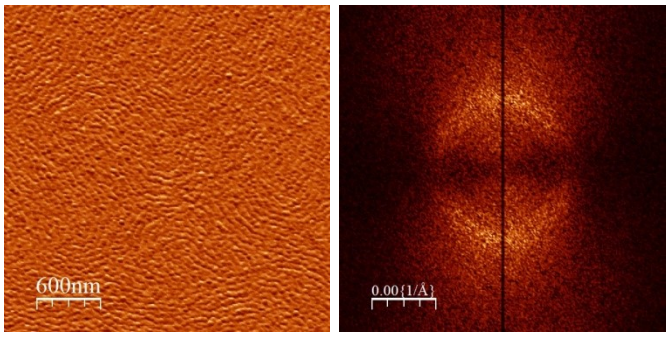

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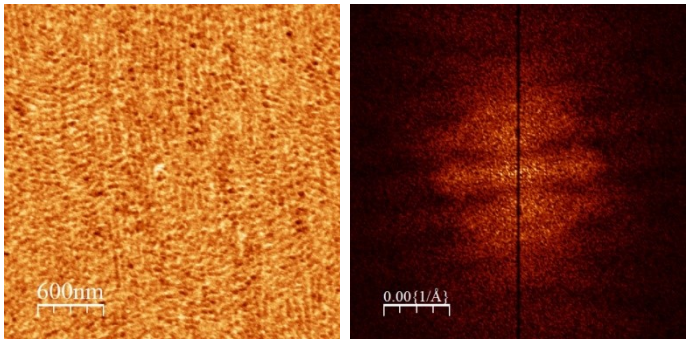
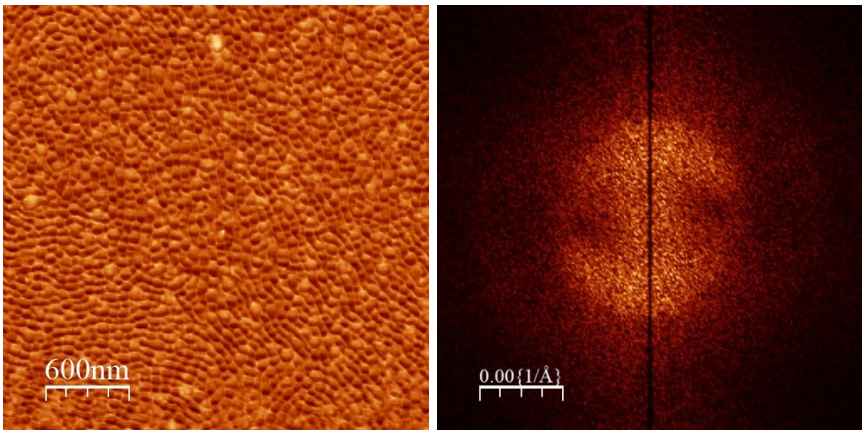


Figure 2: The morphology of samples after solvent annealing with acetone and sputtering with 2 nm of Ag and corresponding images of FFT analysis: (a) presents the sample with heating to 100 °C, (b) presents the sample with heating to 150 °C, (c) presents the sample with heating to 170 °C

(a)



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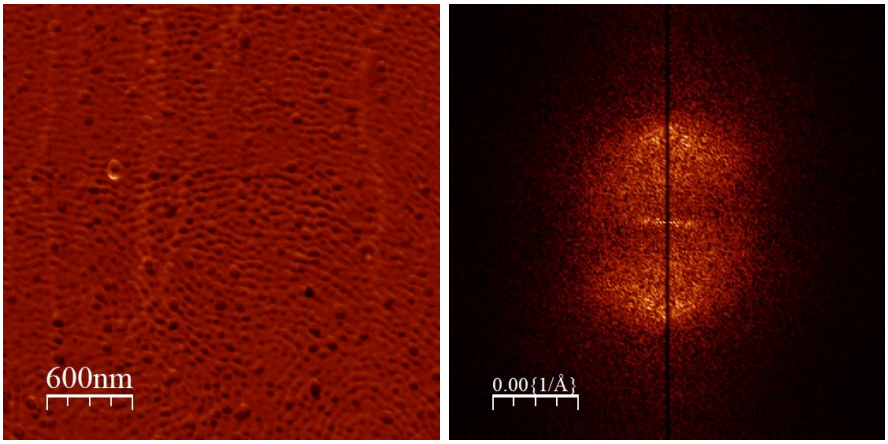
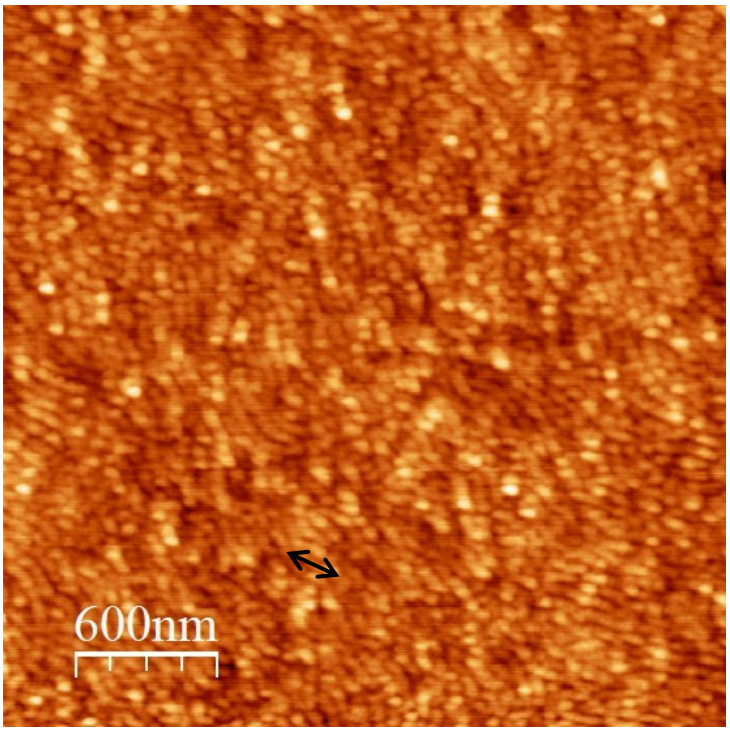


Figure 3: The morphology of samples after solvent annealing with acetone and plasma treatment and corresponding FFT: (a) presents the sample with 5 times treatment , (b) presents the sample with 2 times treatment

To characterize the surface morphology of the samples heated after sputtering of silver the AFM data were used Fig. 4 and Tab. 1.

(a)



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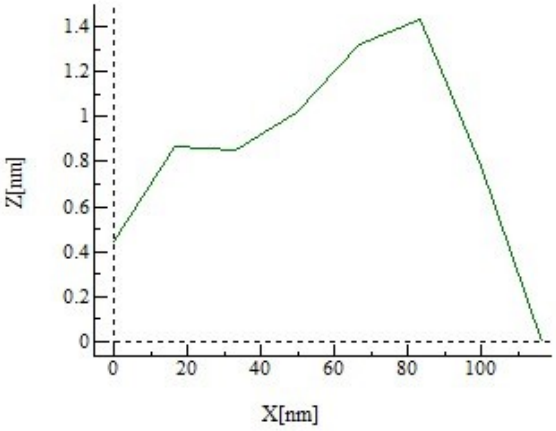

(c) (d)

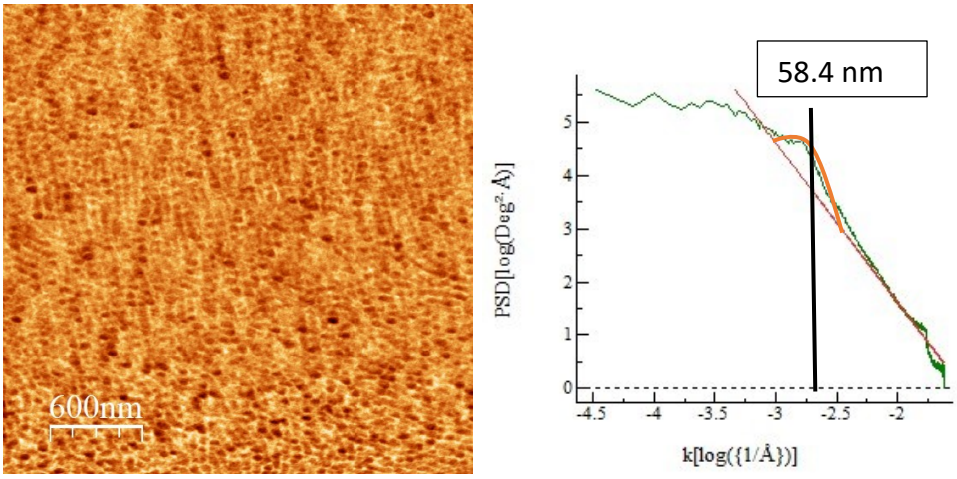

Figure 3: Image (a) was obtained using AFM for measurements of the sample after solvent annealing with acetone, silver sputtering and heating to 150 °C, the profile (b) corresponds to the value of Dptv on lamellar, the phase image (c) obtained during AFM measurements was used to calculate the domain period (d)

Description of the sample	Dom. period, nm	Dptv on lam. , nm	Diam. Cluster, nm
anneal Ace 2,5 h 2nmAg, T = 170C	66,5	1,8	100
anneal Ace 2,5 h 2nmAg, T = 150C	58,4	1,1	100
anneal Ace 2,5 h 2nmAg, T = 25C	63	0,6	60

Table 1: The comparison of values for samples with different temperatures of silver sputtering

5 Conclusion

In this work, the reproducable way of obtaining stable lateral lamellar nanostructures was described. The most appropriate time for solvent annealing with acetone to obtain lateral lamellar structure for PS-b-PMMA 66/67 films according to the experiment is 2.5 hours. Also after annealing with acetone different temperatures for silver sputtering were investigated. And according to results for better structured morphology temperatures for sputtering have range between 150 and 170 °C.

However, more research must be conducted to study the temperature range after the sputtering of silver.