

Exploration of Directed Self Assembly Polymers

Paul Bischoff, Thomas Smith, Robert Pearson, Dale Ewbank
Rochester Institute of Technology
Rochester, NY, USA

ABSTRACT

Directed Self Assembly (DSA) is an attractive alternative to 193i and multiple patterning. Various polymers were investigated to find the possible structures that can be created with them. Previous research was used to determine the process used. Two surface treatments, a polymer brush and hexamethyldisilazane (HMDS) were used to help the polymers phase separate into their respective structure. The first polymer a polystyrene (PS) block polydimethylsiloxane (PDMS) resulted in de-wetting and film non-uniformity that prevented measurement. The second polymer a PS block polyethylene oxide (PEO) resulted in crystallization if the PEO ratio was too high at 40% mole. When the PEO ratio was low enough at 29% mole and on a PS brush polymer via holes 30 nm in diameter were found using phase imaging on an Atomic Force Microscope (AFM). Repeat samples of the via holes de-wetted from the surface likely due to surface contamination preventing the brush polymer from adhering to the surface.

I. INTRODUCTION

As devices get ever smaller there is a need to be able to pattern at smaller and smaller dimensions. At the 10nm node 193i has been used in order to achieve these dimensions with the help of multiple patterning. This, however, is reaching its limits and an alternative is needed. The most popular alternative is currently EUV systems. This is shown to be expensive and with a low throughput. Another alternative is Directed Self Assembly (DSA). It has been shown to have resolutions of 10nm and can be reduced further through multiple patterning. DSA is also inexpensive when compared to EUV and can be used with current 193i tools. The primary drawback to DSA is pattern defects.

II. THEORY

The DSA polymer is a di-block co-polymer. The difference in surface energy between the two blocks is what allows the DSA polymer to rearrange into various structures. The Flory interaction parameter (χ), volume fraction of the polymer (f), and degree of polymerization (N), determines the type of structure formed during phase separation. How these factors interact can be seen in Figure 1. The commonly used structures include the lamellae and cylindrical structures. The lamellae and horizontally oriented cylinders are used for lines and vertically oriented cylinders for via holes.

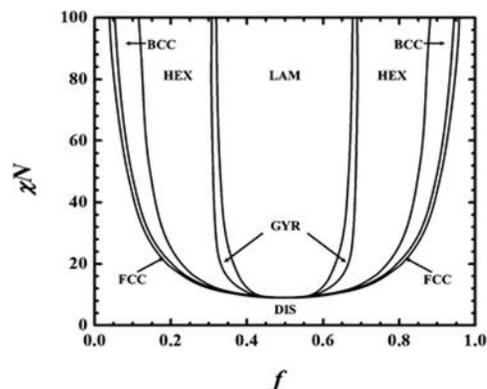


Fig. 1. Phase diagram of di-block co-polymers [4]

The first polymer used was a di-block of polystyrene (PS) and polydimethylsiloxane (PDMS). The molecular weight (MW) of the polymer was 67k-b-22k g/mole. When this polymer is etched the PS will etch away leaving the PDMS which has a silicon group that forms into silicon dioxide. This polymer is expected to form cylindrical structures. The next polymers used were a di-block of polystyrene (PS) and polyethylene oxide (PEO) at 29% and 40% mole. The MW of the 29% mole was 52.5k-b-35.6k g/mole and is expected to create cylindrical structures. The 40% mole is expected to make lamellae structures.

III. PROCEDURE AND RESULTS

The experimental procedures were taken from previous research that used similar polymers [2] [5]. Various surface treatments were used. The first was a hexamethyldisilazane (HMDS) treated surface. This was similar to the trimethoxy silane used in [5]. Next was a carboxylic terminated PS polymer brush. This brush was coated from a 1% solution in toluene at 300rpm for 20 min. It was then baked at 120C for 24 hours and washed in toluene then ethanol to remove any polymer not bonded to the surface. The DSA polymer was then coated from a 1% solution of toluene at 3000rpm for 120 seconds. Annealing of the PS-b-PDMS polymer was done at 170C in a nitrogen ambient for 24 hours. The PS-b-PEO anneal was done for 3 hours in chloroform vapor.

Initially PS-b-PDMS was coated in a 1% Toluene solution onto a native silicon wafer. This resulted in streaks across the surface of the wafer. The initial hypothesis was that particles in the solution caused the streaks in the coating. To test this diatomaceous earth was added to the solution and was gravity filtered. The resulting coating still had the streaks but the coating slightly improved. This showed that particles may have

an effect on the coating but they were not the main problem. Then to test a theory of de-wetting due to difference in surface energy between the polymer and the wafer surface two different coatings were done. One coating was done with a solution of Tetrahydrofuran (THF) instead of Toluene. The other was coating on a PS under-layer. The result of the THF coating can be seen in Figure 3. The coating appeared to have been fixed but under a higher magnification the de-wetting could be seen. The PS under-layer did not result in de-wetting even under higher magnification as seen in Figure 4. The coating also did not appear to be smooth. Both of the coatings appeared to be thicker than the first coatings. The PS under-layer coating was thicker likely because of the under-layer. The thicker coating was likely true for the THF coating because it evaporates faster than the Toluene leaving a thicker layer behind. A solution of 75% Toluene 25% THF was made with the polymer to try and thin the coating. This resulted in de-wetting.



Fig. 2. PS-b-PDMS on HMDS treated wafer de-wetting at 10x magnification

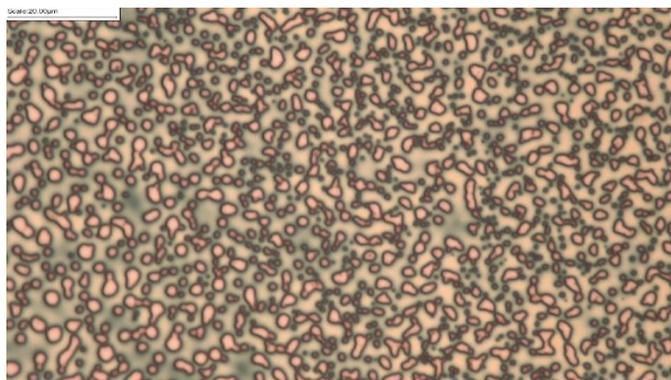


Fig. 3. PS-b-PDMS in THF coating at 100x magnification

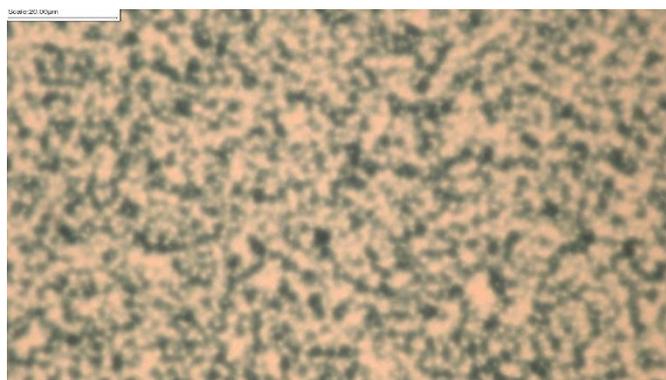


Fig. 4. PS-b-PDMS at 100x magnification

The PS-b-PEO at 40% mole samples crystallized preventing a uniform film from forming. The crystallization can be seen in Figure 5. The films were baked at 200C for 5 min to try and remove the crystals. This temperature is above the melting point of the PEO and glass transition temperature of the PS. This did not result in removing the crystals as they quickly reformed.



Fig. 5. PS-b-PEO crystallization

Both PS-b-PDMS and PS-b-PEO were then spin coated on PS under-layers. None of the PS-b-PDMS coatings were smooth enough to be imaged with the AFM. One of the PS-b-PEO wafers was smooth enough and was imaged under the AFM. The coating was scraped off in small areas and the step height was measured at the edges. It was found to be around 41nm. The image is seen in Figure 6 and the measurement can be seen in Figure 7. The phase image of the surface was then taken on a smaller area of the sample to improve resolution. The phase image measures the elasticity of the polymers. There is enough of an elasticity difference between PEO and PS to create an image. PS-b-PEO samples on the HMDS treated wafers were imaged on the AFM and no structures were seen. This indicates there was no phase separation of the polymer. This can be seen in Figure 8. The width of multiple spots was taken and is shown in Figure 9. The average width was found to be around 30nm.

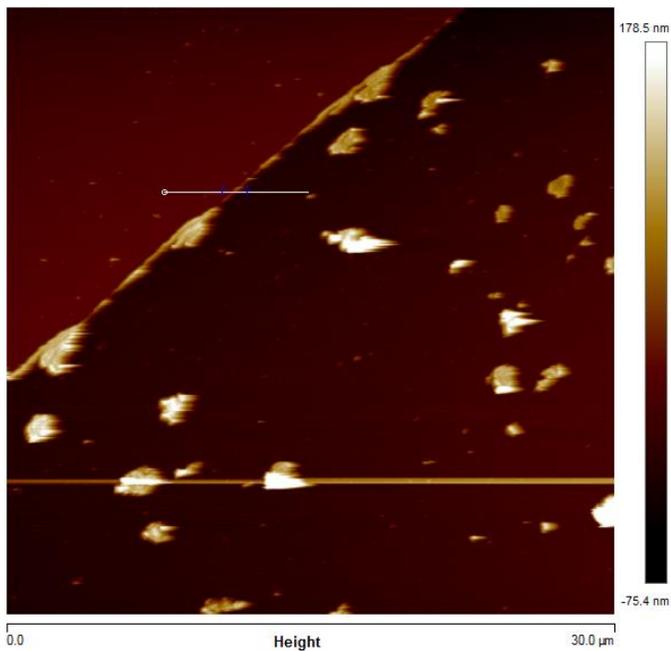


Fig. 6. PS-b-PEO AFM topography map

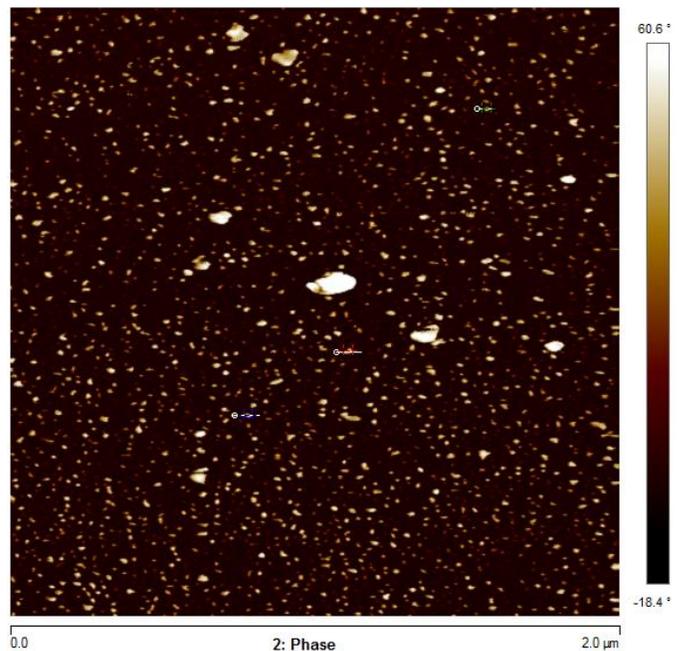


Fig. 8. PS-b-PEO AFM phase image

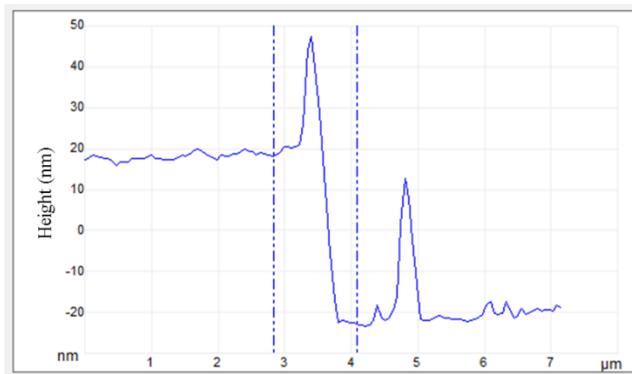


Fig. 7. PS-b-PEO AFM height cross-section

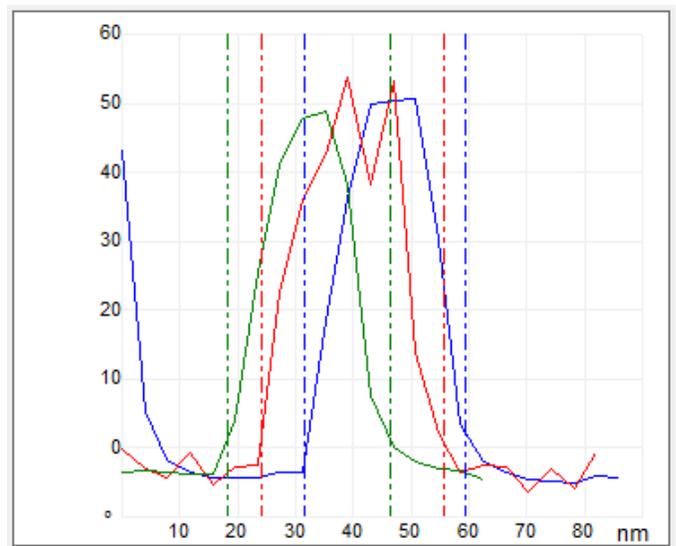


Fig. 9. PS-b-PEO AFM phase cross-section

After AFM imaging etching was attempted on the PS-b-PEO sample. The etch was for 1 minute and resulted in the entire film being etched. A shorter or lower power etch will be needed for etch characterization. More wafers were coated with the PS under-layer and PS-b-PEO polymer at 29% mole for etch characterization. These samples resulted in further etching. This can be seen in Figure 9. The surface cleanliness is suspected to have prevented the PS under-layer from bonding to the surface resulting in the PS being washed away.

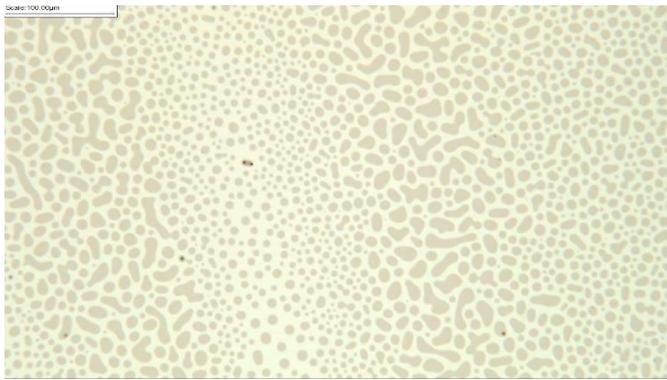


Fig. 10. PS-PEO de-wetting on PS underlayer

IV. CONCLUSION

Many of the coatings had de-wetting issues. The PS-b-PDMS on both the native Si surface and HMDS treated surfaces resulted in de-wetting. The PS surface did help with de-wetting but still had a non-uniform coating. De-wetting also prevented coating PS-b-PEO samples on the PS under-layer. The surface cleanliness likely prevented the PS under-layer from adhering. If the mole % of the PEO is too high the film will crystalize and prevent any phase separation from occurring. The PS-b-PEO samples on the PS brush did have uniform films and 30nm via hole structures were seen.

Addition of Si gratings will allow the polymer to phase separate into a more organized structure.

ACKNOWLEDGMENT

Thank you to the SMFL staff for keeping the SMFL at RIT running so that these samples could be processed. A special thanks to those who helped set up the camera so that a 24hr anneal could be possible. Also thanks to Dr. Guptas for helping with AFM measurements.

REFERENCES

- [1] J. Y. Cheng, *et al.*, "Simple and versatile methods to integrate directed self-assembly with optical lithography using a polarity-switched photoresist," *ACS Nano*, vol. 4, pp. 4815-4823, Aug 2010.
- [2] M. Takenaka, *et al.*, "Formation of long-range stripe patterns with sub-10-nm half-pitch from directed self-assembly of block copolymer," *Journal of Polymer Science Part B-Polymer Physics*, vol. 48, pp. 2297-2301, Nov 2010.
- [3] Courtland, Rachel. "Self-Assembly takes shape." *IEEE Spectrum*. IEEE, 31 Jan. 2012. Web. 07 May 2015.
- [4] Koo, Kyosung, Hyungju Ahn, Sang-Woo Kim, Du Yeol Ryu, and Thomas P. Russell. "Directed self-assembly of block copolymers in the extreme: guiding microdomains from the small to the large." Royal Society of Chemistry, 27 June 2013. Web. 7 May 2015.
- [5] C. Simao, D. Tuchapsky, W. Khunsin, A. Amann, M. A. Morris, and C. M. S. Torres, "Defect analysis and alignment quantification of line arrays prepared by directed self-assembly of a block copolymer," in *Conference on Metrology, Inspection, and Process Control for Microlithography XXVIII*, San Jose, CA, 2014.