

Fabrication of aligned metallic structures based on block copolymer lithography

Yusuke Takahashi

Department of Microelectronic Engineering, Rochester Institute of Technology, 82 Lomb Memorial Dr., Rochester, NY 14623. Email: yxt6709@rit.edu

Abstract—The objective of this project is to fabricate linear metallic patterns based on block copolymer lithography. As the semiconductor industry continue to seek scaling methods, the next breakthroughs in the electronics size barrier are likely to come from devices created out of novel material. Block copolymers have gained considerable potential for nanoelectronics applications such as lithography templates due to its incompatible components self-assemble into well-ordered structures with the scale of 10 to 100nm. In this project, creation of nano-scale structures was attempted via graphoepitaxy, a process where topographically patterned substrate is utilized to control crystallographic orientations. Linear structures of diblock copolymer, Polystyrene-block-poly(2-vinylpyridine) (PS-b-P2VP) were assembled within micro trenches, followed by chemical etching and decoration with gold nano-particles to form metal wires.

Index Terms—Nanofabrication, Block copolymer lithography, Self-assembly, Nanostructures

I. INTRODUCTION

IN the past decades, diblock copolymer have gained considerable potential for nanoelectronics and nanotechnological applications due to its amphiphilic macromolecules self-assemble into well-ordered structures [1]. Among these applications, several researchers have demonstrated used of block copolymer for lithography process with the scale of 10 to 100nm [1-3]. Nanoscale patterns based on self-assembly have been considered as alternative to replace high-resolution lithographic technologies such as X-ray, electron beam and interference lithography to enable continuation of device scaling [1]. International Technology Roadmap for Semiconductors (ITRS) identified directed self-assemblies of molecular structures as a next emerging patterning technology for 16nm half pitch or beyond [4]. The phase segregating block copolymer represents a promising evolutionary step forward in resist technology. These high information content resist materials are designed to make use

of additional nanoscale chemical processes that can be tuned to enhance dimensional control [4]. In the case of implementation to traditional IC fabrication processing, minimum changes will be required because a specific copolymer automatically self-assemble into desired nanoscale structures such as parallel lines for buses or nanoparticles for floating gates. The possibilities for these materials are numerous because of their potential for parallel processing of features along with the simplicity of handling [2].

Many potentials of diblock copolymer for different nanoelectronic applications have been proposed based on their ability to form organized pattern. However, the main challenge of using block copolymer is controlling of nanostructure. Block copolymer alignment has been explored using electric field, shear stress, imprinting, and other methods [6-7]. In this paper, a particular emphasis is made on one processing approach: graphoepitaxy. Graphoepitaxy is a process where topographically patterned substrate is utilized to control crystallographic orientations [1]. As a polymer solution is coated on a substrate with surface relief, block copolymer cylinders forms aligned structures due to controlled confinement. Smith et al originally developed this method in 1978, but it was not until 2001 that graphoepitaxy was utilized to control orientation of block copolymer [1, 8]. This is a prime example of the combined top-down and bottom-up approaches to pattern nanostructures, where both photolithography and molecular self-assembly are utilized. In this experiment, to create aligned linear metallic structures, diblock copolymer, polystyrene-block-poly(2-vinylpyridine) (PS-b-P2VP), was assembled within photolithographically patterned trenches, followed by decoration with gold nanoparticles and chemical etching. The potential application of this method includes nanoscale interconnects; yet it is highly versatile because the user has the control of choosing substrate materials.

II. THEORY

A. Diblock copolymer

A copolymer is any polymer that is built from more than one monomer type. The family of copolymers made from two

Yusuke Takahashi is with the Microelectronic Engineering Department, Rochester Institute of Technology, Rochester, NY 14623 USA (e-mail: yxt6709@rit.edu). This project was supported by RIT's Micro and Nano Fabrication laboratory.

monomer types, A and B, can exist as one of three forms: Random, alternating or block. A random copolymer is characterized by a random ordering of the A and B monomer units in the polymeric chain, such as BBABAAABAABBBAB. Alternating copolymers exhibit a regular alternating pattern of monomer units in the polymeric chain, such as ABABABABAB. Block copolymers represent an unusual class of polymers that are synthesized from two or more distinct homogeneous polymeric blocks. For the case of a diblock copolymer, the structure might correspond to AAAAAAAAAA-BBBBBBBBBB and be represented by the blue and red sections of the polymer chain in Figure 1. Diblock copolymers consist of two chemically different polymer chains joined by a covalent bond. Because of connectivity constraints and the incompatibility between the two blocks, diblock copolymer spontaneously self-assemble into microphase-separated nanometer-sized domains that exhibit ordered morphologies at equilibrium [9]. The chain lengths of the blocks determine the resulting morphology. The size and periods of these microdomain structures are governed by the chain dimensions. Selective processing of one block relative to the other is possible by use of chemical or physical dissimilarities between the two blocks.

Asymmetric PS-*b*-P2VP diblock copolymer was used in this study as shown in Figure 1. The polydispersity index of copolymer is about 1.05 and molecular weights are 32,000 g/mol and 12,500 g/mol for the SP and P2VP respectively. The glass transition temperatures of PS and P2VP are about 100 °C and 140 °C. The P2VP block has a proton acceptor owing to the 2-pyridyl groups, in which nitrogen is not bonded with adjacent carbons, as well as the potential to act as a metal ligand to combine with metal complexes [10]. As the polymer contact with acidic solution (pH < 4.5), a protonation of P2VP occurs, and it alters the polymer structures, swelling of the P2VP block. The protonated P2VP block carries a net positive charge, and thus anionic metallic particles are required for metal loading.

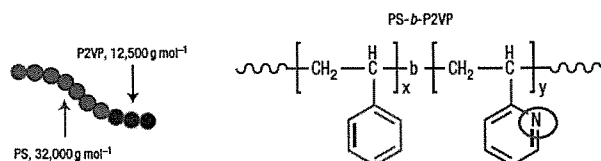


Fig. 1. Structure and molecular weight of the PS-*b*-P2VP used in this study.

B. Graphoepitaxy

Graphoepitaxy is a process in which surface topographies are employed to control crystallographic orientations. The substrate for templating block copolymer self-assembly can be fabricated by standard optical lithography. Spin coating of copolymer solution and annealing on a surface with trenches can lead to self-assembly within a confined area as shown in Figure 2. In the absence of surface reliefs, the block copolymers form fingerprint structures lacking long range alignment and order (Figure 2). The polymers film need to be annealed at a temperature well above their glass transition temperatures (T_g) and are gradually cooled down, allowing

reflow of polymers and organization of polymer structures within the surface topographies [9]. A low process pressure is not required, but recommended to obtain well-ordered morphologies.

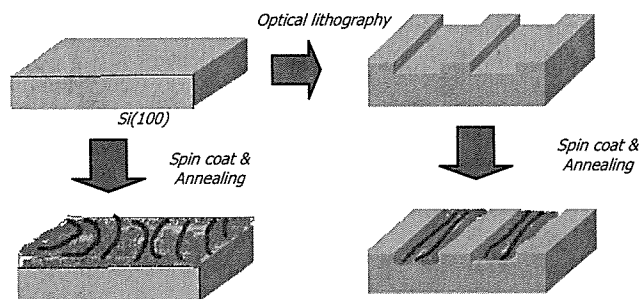


Fig. 2. Schematic diagram of the self-assembly of PS-*b*-P2VP block copolymer on Si(100) surface. Spin coating and annealing of a surface with relief creates self-assembly within confined areas.

C. Metal deposition

A monolayer of spin coated PS-*b*-P2VP does not exhibit clear topography due to its polymer structure where P2VP cylinders are embedded in PS layer. The PS block forms a hydrophobic barrier between the P2VP and the aqueous solution, preventing efficient contact between P2VP and the ionic metals [2]. To induce protonation of P2VP, the polymer-coated substrate is immersed in the HCl (aq.) solution. Upon exposure to acid the P2VP cylinders are swelled up to the surface due to expansion of polymer structures, making direct contact with the ionic metal solution. The negative charge on the anionic metal, AuCl_4^- , leads to an electrostatic bonding with the cationic P2VP surrounded by PS matrix. The hybrid structure is then reduced and PS is removed with a brief chemical treatment using toluene.

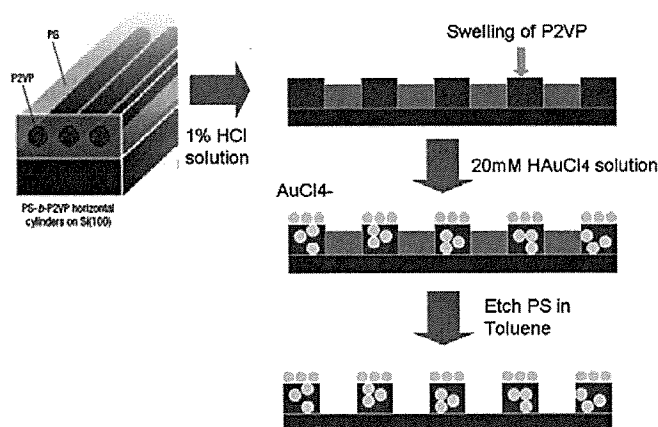


Fig. 3. Schematic diagram of the metal decoration on P2VP of diblock copolymer, PS-*b*-P2VP. The protonation of P2VP causes swelling to the polymer surface, and the ionic metal salt AuCl_4^- become electrostatically bonded to the protonated P2VP surrounded by the PS matrix. The hybrid structure is then reduced and PS is removed in toluene solution.

III. MATERIALS

A. Diblock copolymer solution and ionic metal solution

The asymmetric diblock copolymer PS-b-P2VP (Sigma Aldrich) was obtained with polydispersity index = 1.05 and molecular weights of 32,000 g/mol and 12,500 g/mol for the PS and P2VP respectively. The PS-b-P2VP was diluted with chloroform to make 1% solution. HAuCl_4 (99.999%) was purchased from Sigma-Aldrich.

B. Substrates

A silicon wafer (100) was patterned with a series of 10mm long, 40nm deep channels via photolithography and etching in inductively coupled CHF_3 plasma. Channel widths of 400 and 500nm were produced. Prior to copolymer coating, the substrate was cleaned thoroughly in O_2 plasma to remove photoresist and etch residues. Substrates without surface topographies were also prepared and cleaned in acetone and methanol baths.

IV. EXPERIMENT

All the experiments were performed under ambient conditions at room temperature unless specified. To obtain conformal monolayer of block copolymer solution on the substrates, spin speeds were carefully modified. Polymer film thicknesses were measured using Tencor P2 profilometer, and a spin speed vs. thickness curve obtained. The degrees of polymer spreading were characterized via atomic force microscopy (AFM) for different spin speeds. The spin speed was optimized at 1500 rpm.

The effect of micro-trenches on block copolymer alignment was studied by spin coating polymer solution on the topographically patterned substrate, followed by AFM measurement.

Annealing temperatures and time were investigated to obtain block copolymer self-assembly within the trenches. The patterned substrates coated with polymer solution went through various annealing conditions, altering temperatures and time. A polymer alignment was observed after the annealing at 220 °C for 24 hours.

The chemical etching of polymers was studied by immersing three substrates coated with polymer solution into toluene bath for 1, 3, and 10 minutes. AFM measurements were taken to compare etching effects on each sample.

To decorate P2VP with gold nanoparticles, the polymer-coated substrate was immersed in the gold aqueous metal salt solution for 10 minutes. The metal salt/acid solutions were prepared by mixing 1mL of 20mM HAuCl_4 and 9mL of 1% HCl (aq.). The samples were rinsed with DI water and dried under a nitrogen stream. Toluene etch was performed for 30 seconds to remove PS from polymer matrix.

V. RESULTS AND DISCUSSION

Figure 4 shows the spin speed vs. polymer film thickness curve obtained for 1% PS-b-P2VP dissolved in chloroform, and Figure 5 shows AFM images of block copolymer coated on substrate with 800 rpm and 3000 rpm. A slow spin speeds leads to concentrated polymer orientations and overlapping of polymer structures can be observed. A high spin speed causes high degree of spreading of polymer structures, and spacing between polymers is wider. Modifying the spin speeds as 1500 rpm controlled the thickness of the polymer films to be 60 to 80nm, and a conformal monolayer of copolymer was obtained.

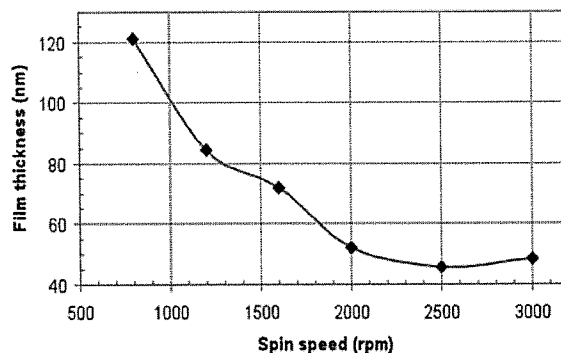


Fig. 4. Spin speeds vs. polymer film thickness curve obtained for 1% PS-b-P2VP in chloroform. The spin speed was optimized to obtain a uniform monolayer at 1500 rpm.

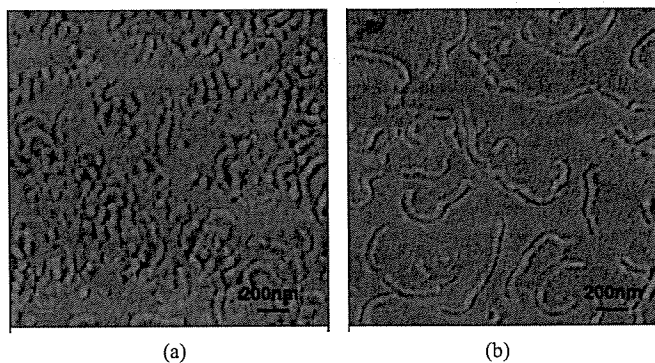


Fig. 5. AFM images of block copolymer PS-b-P2VP coated on substrate with (a) 800 rpm, and (b) 3000rpm. A slow spin speeds causes overlapping of copolymers, and a high spin speeds leads to more spreading polymer structures.

Figure 6 shows AFM images of 400nm wide and 40nm deep micro-trenches created via optical lithography and deep RIE, and block copolymers spin coated on the topographically patterned substrate. The fingerprint self-assembly of block copolymers was still observed, and self-alignment does not occur in the absence of proper annealing process.

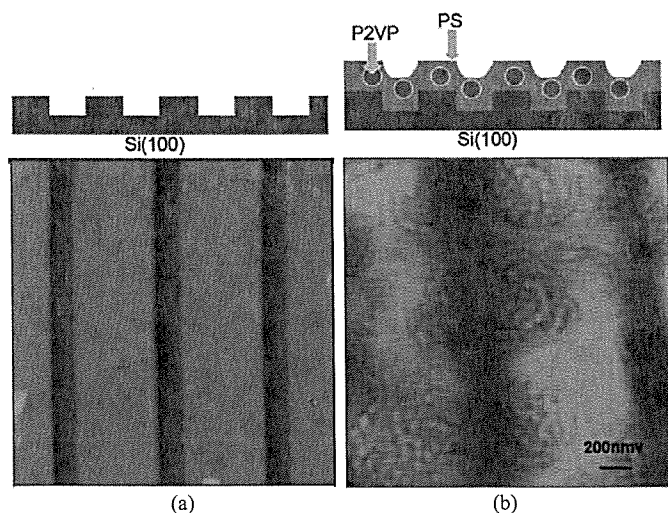


Fig. 6. AFM images of (a) 400nm wide and 40nm deep micro-trenches created on substrates, and (b) block copolymer coated on substrate with micro-channels. The self-assembly of block copolymer does not occur in absence of the annealing.

Figure 7 shows AFM images of block copolymers self-assembled within the micro-channels after an annealing at 220 °C for 24 hours under atmospheric pressure. In the three dimensional picture, the green lines indicate edges of micro-trench, and the red lines indicate self-aligned P2VP polymer structures. The width of P2VP was measured as 40nm. Annealing above the glass transition temperature of copolymers and gradually cooling down create a reflow of the polymer networks into the trenches, organizing self-aligned structures.

Figure 8 shows AFM images of block copolymer spin coated on substrates and etched in toluene solutions for 1, 3, and 10 minutes. A high degree of P2VP concentration was observed after 1 minute etching because PS was removed from the top surface, and 3 minutes etching removes most of P2VP, creating wider spacing between polymers. After 10 minutes of toluene etching, no structure was observed, removing all the copolymers. It has been cleared that toluene etches two polymers at dissimilar etch rates. To remove all the PS and retain a high concentration of the P2VP, the etch time was optimized as 30 seconds.

VI. CONCLUSION

It was the purpose of this investigation to fabricate aligned metallic structures via block copolymer self-assembly. Alignments of polymer structures within photolithographically patterned trenches have been demonstrated using graphoepitaxy. Spin coating was modified to obtain a monolayer of copolymer film. The effects of annealing process on polymer alignment and the optimal annealing conditions were studied. The chemical etching of block copolymer was investigated to selectively remove one kind of polymers from a mixed polymer matrix. Additional studies need to be performed regarding same copolymers with smaller molecular weight, and different conductive materials such as

aluminum, copper, or CNTs.

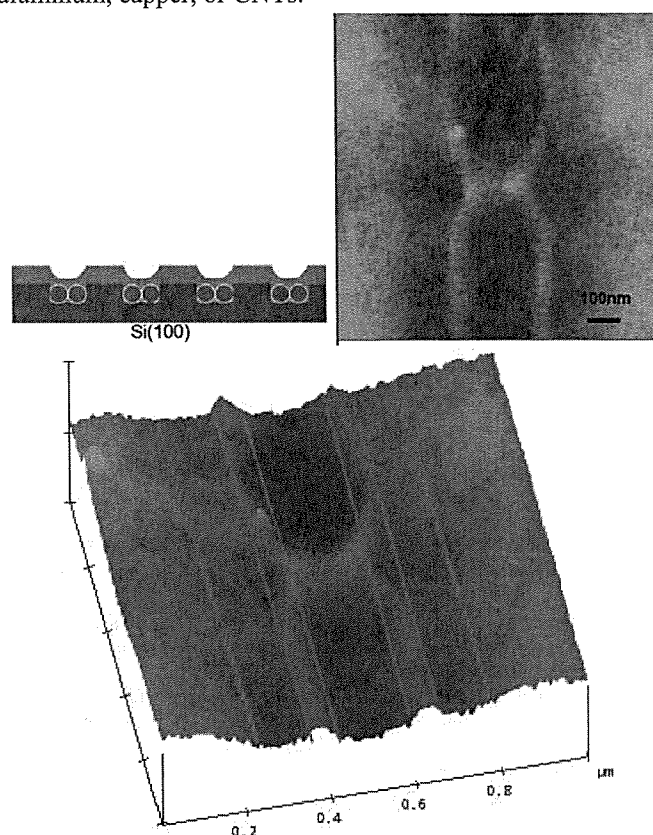


Fig. 7. AFM images of block copolymers self-assembled within the micro-trenches after an annealing at 220 °C for 24 hours under atmospheric pressure. The width of aligned P2VP was measured as 40nm indicated with red lines. Annealing above T_g of copolymers and gradually cooling down allow the polymer networks to reflow into the trenches and organize self-alignment.

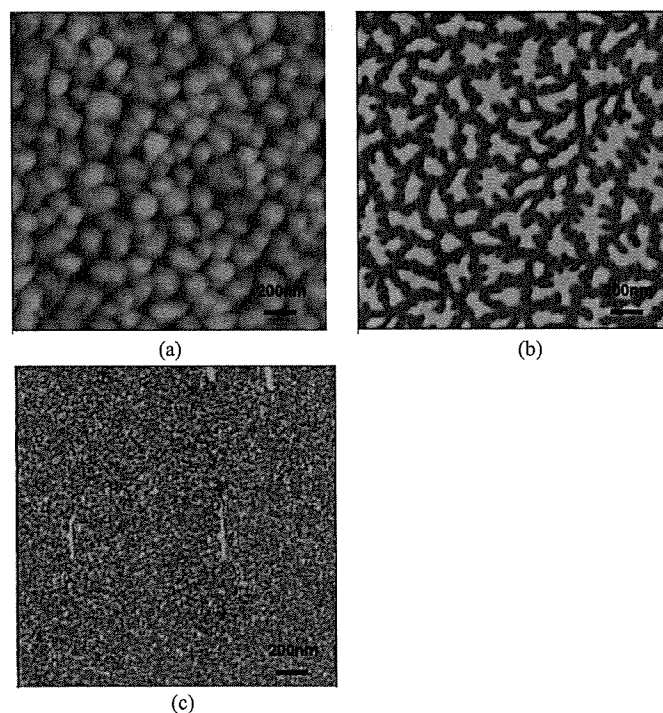


Fig. 8. AFM images of block copolymer PS-b-P2VP spin coated on substrates and etched in toluene solution for (a) 1min, (b) 3min, and (c) 10min. Toluene etches PS faster than P2VP, but 10min etch removed all the copolymers.

ACKNOWLEDGMENT

Author thanks Prof. Ewbank, Prof. Mariotti, and Prof. Lu for project supports and advices, and Prof. Gupta and Dr. Bai for AFM training and variable discussions. Author also thanks Kenneth Fourspring and CK Chen for their help on substrate preparation. The processes were performed in SFML at RIT, and author greatly appreciates SMFL staff for technical assistance and equipment support.

REFERENCES

- [1] Park, C., Yoon, J. and Thomas, E. L. "Enabling nanotechnology with self assembled block copolymer patterns," *Polymer* vol 44, pp. 6725-6760, 2003.
- [2] J. Chai, D. Wang, X. Fan, and J. M. Buriak, "Assembly of aliened linear metallic patterns on silicon," *Nat. Nanotechnol.* vol 2, pp. 500-506, 2007.
- [3] M. R. Hammound and E. J. Kramer, "Edge effects on thermal disorder in laterally confined diblock copolymer cylinder monolayers," *Macromolecules* vol 39, pp. 1538 – 1544, 2006.
- [4] International Technology Roadmap for Semiconductors - Lithography, Santa Clara, CA: Semiconductor Industry Association, Lithography pp 27, 2007
- [5] K.Schmidt, H. Schoberth, M. Ruppel, H. Zettl, H. Hansel, T. Weiss, V. Urban, G. Krausch, A. Boker, "Reversible tuning of a block copolymer nanostructure via electric fields," *Nat. Materials.* Vol 7, pp 142-145, 2008.
- [6] T. L. Morkved, M. Lu, A. M. Urbas, E. E. Ehrichs, H. M. Jaeger, P. Minsky, T. P. Russell, "Local Control of Microdomain Orientation in Diblock Copolymer Thin Films with Electric Fields," *Science* 273, 931-933, 1996.
- [7] Xu, H. et al. "Flow-enhanced epitaxial ordering of bruch-like macromolecules on graphite," *Langmuir* 22, 1254-1259, 2006.
- [8] Smith HI, Flanders DC. *Appl Phys Lett*, vol 32, ppt 349, 1978.
- [9] D. H. Adamson, "Block Copolymer Lithography: Periodic Arrays of 10^{11} Holes in 1 Square Centimeter," *Science*, vol 276, 1401-1404, 1997.
- [10] Aizawa, M. Buriak "Nanoscale patterning of two metals on silicon surfaces using and ABC triblock copolymer template," *J. Am. Chem. Soc.* vol 128, 8877-5886, 2006.

Yusuke Takahashi is originally from Chiba, Japan, received a B.S. degree in Microelectronic Engineering from Rochester Institute of Technology in 2008. He obtained co-op work experience at Infotonics Technology Center in Canandigua, NY, and also worked as a research assistant at Micro and Nano Manufacturing laboratory at RIT.