Block Copolymer Self-assembly: Lithography, Magnetic Fabrication, and Optimization

by

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Abstract

Block copolymer (BCP) self-assembly is attractive because it provides nanoscale long-range ordered structures in a massive quantity. The capability of generating features with size as low as 5 nm is of particular interest in semiconductor fabrication since current photolithography has reached its resolution limitation and the other competing technologies are either too slow such as e-beam lithography or too expensive such as EUV system. In this thesis, BCP lithography is utilized to fabricate magnetic nanostructure and the corresponding magnetic properties are explored.

The polystyrene-\textit{b}-polydimethylsiloxane (PS-\textit{b}-PDMS) diblock copolymer with different molecule weight is used to generate various sizes of robust silica pattern after solvent annealing and reactive ion etching. Pattern transfer methods are developed to convert the silica pattern into functional materials, including magnetic materials like cobalt, Co/Pd, FePt and CoFeB magnetic tunnel junctions (MTJ), and MoS\textsubscript{2} monolayers. For magnetic nanowire arrays, the interactions between neighboring wires are investigated. For perpendicular MTJ nanopillar arrays, the size-dependent switching behavior and magnetostatic effects between two layers are analyzed. MoS\textsubscript{2} monolayers are patterned into features such as nanodots, nanorods and nanomeshes and the corresponding photoluminescence are characterized.
Finally, machine learning and deep learning algorithms are the first-time ever demonstrated to model the BCP self-assembly process. The built model is able to recognize different BCP patterns and predicting the resulting morphology and pattern quality based on experimental process parameters. With this model, the BCP self-assembly can be further optimized toward industrial-grade production.

Thesis Supervisor: Caroline A. Ross
Title: Toyota Professor of Materials Science and Engineering
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CHAPTER 1

Introduction

1.1 Motivation and Thesis Overview

Self-assembly is a special gift of nature that an ensemble of disordered individual components spontaneously forms an organized structure, as a consequence of specific, local interaction among the components. Block copolymer (BCP), as one of the many self-assembly systems, has demonstrated the capability of generating a variety of well-ordered periodic structures at the scale ranging from 5 to 100 nm [1–5]. This is of particular interest in semiconductor industry because the current photolithography has encountered the bottleneck of resolution, and BCP self-assembly is one of the emerging technologies that solves the issue. Some other potential candidates are electron beam (e-beam) lithography and extreme ultraviolet lithography (EUV). Compared with e-beam lithography, BCP self-assembly possess the advantages of high scalability and high throughput, as the pattern for a 300 mm wafer can be done in minutes using BCP self-assembly while it would take up to years by e-beam system depending on resolution, feature size, dose and beam current. On the other hand, although EUV has the most similar working mechanism as photolithography that guarantees the throughput and the integration to the production line, the cost of EUV tools is enormous. A single EUV instrument costs a hundred million dollars, which is three times higher than
the current system, not mentioning billions of dollars spent in developing. By contrast, BCP itself is inexpensive, and because of the simple processing, the required apparatus is much more cost-effective.

As the BCP self-assembly provides the desired pattern, transfer methods are also required in order to convert the BCP morphology to functional materials. In chapter 3, three pattern transfer methods have been developed for polystyrene-block-polydimethylsiloxane (PS-b-PDMS) diblock copolymer, including the Damascene, liftoff and ion-beam etch process. Magnetic nanowires and nanodots were demonstrated with these pattern transfer processes and compared in term of structural and magnetic properties.

Magnetic based devices have been an important part for information storage and sensing in consumer electronic industry for decades. Although having the benefits of high capacity, high reliability and low fabrication cost, they suffer from the low energy efficiency and low processing speed. The recent development in spintronics [6, 7], a portmanteau meaning of spin transport electronics, has not only addressed these issues but further exhibited the potential ability in logic. For example, the prototypes of racetrack memory [8, 9] and magnetic random access memory [10–13] have shown the promising writing and read performance with low energy consumption at the order of 100 femto-Joule [14, 15]. Domain wall based devices were demonstrated to perform gate-like functionality and logic computing. [16–18] In these applications, the fabrication of magnetic nanodots and nanowires are necessary. Nevertheless, because of the limitations in lithography, large-area, high density arrays of device in nanoscale size were usually difficult to obtain, and thus BCP self-assembly has become a great tool to fill the gap. This also enables the collective characterization of magnetic properties using magnetometry, such as alternating gradient magnetometer and vibrating sample magnetometer. In chapter
4, the high-density arrays of magnetic nanowires with in-plane and out-of-plane anisotropy are realized using BCP lithography. The size-dependent interactions between adjacent nanowires are analyzed and reported. In chapter 5, magnetic tunnel junction nanopillar arrays with the diameter of 25 nm and 64 nm are patterned with BCP lithography, and the reversal behavior and thermal stability are studied in detail.

2D materials (single layer materials) is another potential candidate to be used in future electronics. Since being discovered in 2004 [19], graphene has attracted extreme large attention because of its extraordinary intrinsic material properties. For example, it has the known highest carrier mobility of 200,000 cm²/V·s, which is about 400 times higher than silicon. Moreover, the thermal conductivity and mechanical strength are also the highest among other materials to date. Other 2D materials are of interest as well since they may obtain comparable properties as graphene but with an existing bandgap, making them more suitable for electronic application. BCP self-assembly is incorporated here to adjust the properties of 2D materials. In chapter 6, we show the changing in photoluminescent characteristics of nanopatterned molybdenum disulfide (MoS₂) monolayer. Its carrier mobility can also be enhanced using crested substrate patterned by BCP lithography.

Although BCP self-assembly is promising in lithographic application, a few problems remain to be conquered in order to transit the laboratory demonstration into industrial production. One of them is high defect density. Intrinsic BCP morphology tends to have defects as the randomness is inevitable in thermodynamically-driven self-assembly. The other issues in long-range order, edge roughness and uniformity are also critical. Thus, finding an optimal self-assembly process condition that results into low defect, long-range order pattern is
important. Researchers have been using theories like thermodynamic and polymer kinetics to understand the self-assembling behavior, and developed self-consistent field theory (SCFT) to simulate the BCP evolution [20]. However, the gap between theory and practical experiment still exists, and it is infeasible and inefficient to experiment all the potential combination of process parameters to find the optimal condition. In chapter 7, a pioneering approach, machine learning and deep learning, has been utilized to model the BCP self-assembly process. The resulting BCP morphology and pattern quality can be predicted by the machine learning model with given process parameters and the optimal condition can be found by grid searching through the parameter space. Moreover, the potential physical relationship between the process parameters and results would be able to inferred from the modeling.

In the last chapter of the thesis, the works in exploring block copolymer self-assembly are summarized, including developing pattern transfer methods, the applications in magnetic nanodevice and 2D materials, and the self-assembly process optimization. A few suggestions for the future work are provided at the end.

1.2 Block Copolymer Lithography

1.2.1 Self-assembly Behavior

Block copolymers (BCPs) are a class of polymers that two or more distinct polymer chains are connected together by covalent bond [21]. If the polymer chains are immiscible to each other, phase separation is desired at the temperature below the order-disorder transition temperature. Macro scale phase separation is prohibited as the polymer chains are still bonded together; instead, BCP will self-assemble into periodic structures as the microphase separation happens [21]. For a
diblock copolymer, which has two different polymer chains linearly bonded together, several bulk morphologies are available, including spheres, cylinders, gyroid and lamellae. Figure 1-1 shows the schematic of a diblock copolymer and the potential bulk morphologies.

![Diblock Copolymer Schematic](image)

Figure 1-1 The schematic of a linear diblock copolymer and its potential bulk morphologies [22].

Flory-Huggins model is used to understand the thermodynamic driving forces that cause the spontaneous BCP phase separation. In this model, the change in Gibbs free energy of mixing two dissimilar polymers is given by

\[
\frac{\Delta G_{mix}}{k_B T} = \frac{f_A}{N_A} \ln(f_A) + \frac{f_B}{N_B} \ln(f_B) + f_A f_B X,
\]
where $f$ is the volume fraction, $N$ is the repeat units of each polymer, $\chi$ is the Flory-Huggins interaction parameter, $k_b$ is the Boltzmann constant and $T$ is the absolute temperature. As the universe tends to minimize the free energy, if the change in the energy term is greater than zero, the mixing these two polymers is unfavorable, and therefore the spontaneous phase separation happens. The Flory-Huggins parameter here describes the dissimilarity between two chemistries and is formulated as

$$\chi = \frac{V_{seg}(\delta_A - \delta_B)^2}{RT},$$

where $V_{seg}$ is the actual volume of a polymer segment, $\delta$ is the Hildebrand solubility parameters and $R$ is the gas constant. In practice, the product $\chi N$ is used to estimate the segregation strength of two polymer blocks. If $\chi N < 10$ (as $f=0.5$ in the bulk system), two polymer chains would be intermixed and shows a disordered morphology, and if $\chi N \gg 10$, there would be a strong segregation force and the interphase region between two polymers would be narrow. If $\chi N \sim 10$, which is around weak segregation limit, the two polymers would be slightly mixed at the interface and the composition profile would be sinusoidal [21]. According to this rule, if one would like to obtain the structure of small feature size (small $N$) using diblock copolymer, selecting the two polymer blocks with a high Flory-Huggins parameter is required. Figure 1-2 shows the phase diagram of diblock copolymer morphology under different $\chi N$ and $f_A$, as (a) is predicted by self-consistent mean-field theory (SCFT) and (b) is the experimental result from poly(isoprene-styrene) diblock copolymer system. The discrepancy between the numerical modeling and the experiment is resulted from the differing properties of the two blocks (there is no B block that is the exact opposite of an A block in reality) and the additional constrains caused by experimental process.
Figure 1-2 Phase diagrams of the bulk morphology in diblock copolymer system which is (a) predicted by SCFT, (b) obtained experimentally. (S: sphere, C: cylinder, L: lamellae, PL: perforated lamellae, G: gyroid, CPS: close-packed sphere) [23].

It is important to point out that for lithographic application, BCPs are not used in bulk, but as thin films [24]. The typical morphologies can be obtained with a diblock copolymer thin film are hexagonally packed spheres, cylinders, perforated lamellae and lamellae, as the first three shown in figure 1-3. When BCP is confined to a thin film, the incurred constrains such as the surface energies, film thickness and other geometrical confinements, will also largely affect the resulting morphology of self-assembly [25–28]. It is critical to find the proper process parameters in order to acquire desired BCP pattern for lithography.
1.2.2 Pattern Transfer Methods

As the BCP itself usually does not have desired functionality, it is essential to develop pattern transfer methods to convert the BCP patterns into other functional materials. From past to now, people have demonstrated many kinds of pattern transfer methods depending on the polymer species and the target applications.

A large amount of works was done it in a subtractive manner. The very first one was proposed by S. Zhu et al, in which they made polystyrene-poly-2-vynil pyridine (PS-b-P2VP) nanostructure on top of a 30 nm cobalt film and then used Ar plasma to sputter and transfer the polymer pattern into the cobalt film [29]. After that, lots of more improved experimental work has been carried out by several research groups. Aimed at industrial use in data storage, one group at Toshiba was using poly(styrene-\text{-}b\text{-}methyl methacrylate) PS-\text{-}b\text{-}PMMA as a template to pattern CoCrPt and FePt [30, 31]. They spin-coated PS-\text{-}b\text{-}PMMA onto the magnetic thin film, and then after PMMA domains were removed by RIE, they filled the voids with spin-on glass to serve as a hard etch mask for subsequent ion-milling. The magnetic nanodots made with this method were more uniform and presented a
good ordering. These are important keys to realize the idea of bit patterned media (BPM), in which each bit of data is stored according to the magnetization direction in a discrete magnetic nanostructure. On the other hand, Cheng, et al. had used polystyrene-β-polyferrocenyldimethylsilane (PS-β-PFS) block copolymer to pattern magnetic thin films [32, 33]. Since most magnetic metals do not chemically react with common radicals in reactive ion etch (RIE), nor have volatile product after plasma etching, a special design of pattern transferring process was implemented, shown in figure 1-4. In her experiment, a silica and a tungsten layer were initially placed between PS-β-PFS BCP thin film and the target magnetic film. After self-assembly, the PS block was removed by O₂ plasma, and the remaining PFS pattern was transferred into silica layer using a CHF₃ plasma. This pattern was further transferred into the tungsten layer by CF₄/O₂ plasma etching, and finally patterned the magnetic film by Ar ion-milling. This process had used to pattern NiFe/Cu/CoFe multilayers as well as CoCrPt/Ti perpendicular magnetic films, and the magnetic measurement results showed that the layered structure had been successfully preserved in these processing steps, which is promising for the future magnetic applications. In contrast, quartz pillars are much easier to fabricate. Yang et al showed that by inserting a 3 nm Cr layer between BCP film and quartz, the self-assembled BCP structure was firstly transferred to Cr layer using Ar ion-milling, and the Cr nanostructure can behave as the hard mask in the subsequent etching of quartz using RIE [34, 35]. These quartz pillars can also be utilized for BPM fabrication afterwards.
Pattern transfer can also be done in an additive manner. Xiao et al. fabricated cobalt dot arrays by incorporating the additive patterning process [36]. They used the PS-\textit{b}-PMMA to form the BCP template, and after removing the PMMA block, they directly sputtered a 10 nm cobalt thin film onto it. Then the lift-off process was carried out using either dry or wet etching methods. Although there were some missing dots in the wet etching one, the experiments still showed promising results in BCP patterned BPM. In addition, Jung et al. demonstrated transfer of grating patterns, rings and dot arrays into several metals including Ti, W, Pt, Co, Ni, Ta, Au and Al by a damascene-like process using polystyrene-\textit{b}-
polydimethylsiloxane (PS-\textit{b}-PDMS) [37]. In this process, a film was deposited over the block copolymer mask and planarized and etched back using a reactive ion etch, leaving arrays of dots and lines at the locations of pores in the pattern. Moreover, people have also used electrodeposition to grow freestanding nanorods and nanowires using BCP template [38–41].

There are also processes where a material is precipitated directly within microdomains. For example, the metal salts such as Au can be loaded into polyvinylpyridine blocks by immersing the BCP film into hydrochloric acid (HCl) aqueous solution with anionic metal precursor (AuCl$_4$). And then a subsequent plasma etching would remove the BCP template and leaving the metal nanostructure exactly replicating the morphology of polyvinylpyridine blocks [42]. Sequential infiltration synthesis is another similar approach that use atomic layer deposition to introduce materials such as Al$_2$O$_3$, ZnO and W into PMMA blocks, which can be used as a robust mask for the subsequent patterning [43, 44]. In general, these chemical processes have shown excellent results but offer limited filling factor, purity, and metal compositions.

1.3 Properties and Applications of Magnetic Nanostructures

1.3.1 Magnetic Nanowires

Magnetic nanowires have attracted great attention recently because of the development in domain wall (DW) based device. DW is an interface between two magnetic domains that have different if not opposite magnetizations. In bulk material, Bloch and Néel wall are the two main DW configurations, depending on the competition between demagnetizing energy and exchange energy. If the material is thick enough, Bloch wall is energetically favorable since the system would like to minimize the dominated exchange energy. On the contrary, if the
material is thin enough, the high stray field would result in high demagnetizing energy, making the Néel wall more stable. Figure 1-5 shows the schematic configurations of both Bloch wall and Néel wall and the energy variation of these two kinds of DW under different material thickness.

![Schematic configurations of Bloch wall and Néel wall](image)

Figure 1-5 (a) The schematic structure of Bloch wall and Néel wall. (b) The total energy of Bloch and Néel wall with different film thickness (top). As the system favors the configuration with lower energy, Néel wall is dominated when the film is thinner than 40 nm while the Bloch wall is preferred when the film is thicker than 40 nm. The bottom diagram shows the DW width as a function of film thickness [45].

In thin film wires with in-plane magnetization, three types of DW configurations are commonly reported: transverse walls, asymmetric transverse walls, and vortex walls, depending on the ratio of the width/thickness of the wire and the exchange length of the material. A vortex wall (VW) which minimizes the stray field is favored in thicker and wider wires, whereas thinner and narrower wires favor a transverse wall (TW) which minimizes exchange energy, as shown in
An asymmetric transverse wall can be viewed as an intermediate state between a VW and a TW. In comparison, circular wires with small diameter are reported to have transverse walls and those with large diameter have a vortex-like curling wall structure. The present article focusses on the regime of narrow nanowires in which the transverse wall dominates.

Figure 1-6 Magnetic configuration of (a) transverse wall and (b) vortex wall in thin film wire. (c) Phase diagram of transverse wall and vortex wall under different thin film width and thickness [46].
Figure 1-7 (a) Example of magnetic domain wall logic circuit. The DW is driven by a rotating magnetic field and the results are measured by MOKE at position I, II, III and IV [17].

One of the applications that using magnetic nanowires is domain wall logic, proposed by Allwood et al [17]. By carefully design the wire geometry, several logic functionalities including Fan-out, Cross-over, NOT and AND can be realized. Figure 1-7 (a) shows the example of magnetic logic circuit. To operate the system, a counterclockwise rotating field is applied at the frequency of 27-Hz and the computing result was detected using MOKE. Figure 1-7 (b) shows the MOKE signals at position I to IV in the circuit and we can see that the AND gate behaved quite well as the signal at position IV was the summation of the signal at position II and III.
Racetrack memory is another promising application that takes the advantage of magnetic nanowires [8, 9, 47, 48]. DWs are formed in the nanowire between two domains with opposite directions, and the presence/absence of a DW are used to represent data bits of 0 or 1. Instead of using magnetic field, the DWs, as well as the data bits, are moved by nanosecond wide current pulses. The data bits are written and read by magnetic tunnel junctions. Figure 1-8 shows the schematic of racetrack memory. Compared to traditional hard disk drives (HDD), racetrack memory does not have mechanical reading and writing head, so it largely accelerates the data processing speed in random access. The current-driven mechanism also makes it more compatible to CMOS technology.
1.3.2 Magnetic Nanodots

The properties such as coercivity of magnetic nanoparticles are greatly affected by the particle size. For a large particle, the magnetic switching is dominated by domain wall motion, which is similar as in a bulk material. Nevertheless, things become interesting when the particle size is small enough that can no longer sustain the existence of domain wall. With the assumption of single
domain particle with uniaxial anisotropy and coherent switching, Stoner-Wohlfarth Model can be used to describe the reversal behavior. The energy of the system (figure 1-9(a)) is

$$E = K_u V \sin^2(\varphi - \theta) - \mu_0 M_s V H \cos \varphi,$$

where $V$ is the switching volume of particle, $M_s$ is the saturation magnetization, $\mu_0$ is the vacuum permeability, $K_u$ is the magnetic anisotropy energy and $H$ is the magnetic field. Noted that there are two volume parameters defined in magnetic particle, one is the physical volume and another one is the switching volume, which is the activated magnetic volume of a reversal behavior. Due to the assumption of coherent switching in Stoner-Wohlfarth model, these two volumes are considered to be the same. Figure 1-9 (b) shows the hysteresis loops predicted by this model that strongly depend on the angles between the magnetic field and easy axis. In practice, some other incoherent switching processes such as curling, buckling, fanning are more likely to happen if the particle is large enough to support inhomogeneous magnetization.

Figure 1-9 (a) Schematic single domain magnetic particle system and (b) the predicted hysteresis loops of Stoner-Wohlfarth model [49].
Thermal stability is an important factor that quantifies how long the magnetization can sustain in a magnetic particle. According to Arrhenius–Néel formulation, the rate of magnetic reversal,

\[ r = f_0 \exp\left(\frac{-\Delta E}{kT}\right), \]

is defined by the probability per unit time of crossing the energy barrier \( \Delta E \), where

\[ \Delta E = KV(1 - H/H_0)^2. \]

\( f_0 \) is the attempt frequency for barrier crossing and typically on the order of \( 10^9 \) s\(^{-1} \). \( k \) is Boltzmann’s constant and \( T \) is temperature in Kelvin. As suggested by these two equations, if the particle size is too small, the energy barrier for the particle to switch would be low. If the energy barrier is lower than \( 20 \, kT \), the particle will exhibit superparamagnetic behavior, for which the particle is switched at the rate of 1 Hz. For memory purpose, an energy barrier of \( \sim 40 \, kT \) is desired, implying the particle would switch lower than once over 10 years.

Bit patterned media is a potential application that uses magnetic nanodots as the bit storage media. Compared to the current HDD that uses tens of grains (~8 nm/grain) to save 1 bit, the bit patterned media can largely increase the areal density up to 20 times. Figure 1-10 shows the schematic that compares the structure of traditional HDD and bit patterned media.

Magnetic random access memory is an application that uses magnetic tunnel junctions (MTJs) as the storing units, where each MTJ can be considered as a magnetic nanodot. It was initially demonstrated using magnetic materials with in-plane anisotropy and using spin-transfer torque to perform switch. However, it suffers from the variability in shape anisotropy and the high switching current density. As a result, researchers have shifted to materials with perpendicular anisotropy (with the easy axis in the out-of-plane direction) [13, 50, 51], which
allows the device to have a smaller footage and a lower energy consumption. Recent development in spin-orbit torque switch can potentially improve it even further [52].

Figure 1-10 Schematic of the storages in HDD and bit patterned media [53].

1.4 Machine Learning and Deep Learning Techniques for Analysis of BCP Self-assembly

Achieving BCP pattern qualities that meet industrial standard such as low defect density and long-range ordering are important keys to transit the laboratory demonstration into industrial production. Instead of heuristically search in the potential parameter space to find the optimal condition that results into good BCP pattern, we can utilize machine learning and deep learning algorithms to help us. There are many algorithms have been developed for different types of problems, and here artificial neural network and ridge regression are chosen to model the BCP self-assembly process.
1.4.1 Artificial Neural Networks

Thanks to the advance in graphics processing unit, artificial neural network has been rapidly developed in the last decade [54]. It has become the most powerful predicting model and achieved numerous successes in various domain areas such as image and voice recognition [55–57], robotics, and medical diagnosis [58–60]. There are three main classes of artificial neural network: the feedforward neural network (basic structure), the convolutional neural network and the recurrent neural network. Their basic structure and components are introduced in the following paragraphs respectively.

a. Feedforward neural network

Figure 1-11(a) shows the basic structure of a neural network, consisting an input layer, an output layer and hidden layer(s). In each hidden layer, there can be an arbitrary number of nodes (neurons), which is analogous to axons in a biological brain. Each connection (synapse) between nodes can transmit a signal to another node. The receiving (postsynaptic) node can process the signal(s) and then signal downstream nodes connected to it. More specifically, each node collects the weighted sum of the incoming values from the previous layer and then applied an activation function before passing to the next node, as shown in figure 1-11(b). Mathematically, the calculation in a hidden layer is formulated as

\[ Y = f(WX), \]

where \( X \) is the feature vector from the input layer or the incoming signal from the previous hidden layer, \( W \) is the weight matrix, \( f \) is the activation function, and \( Y \) is the output. It has been proven that any continuous function can be approximated by a single hidden layer neural network. The weight matrix here is a collection of variables that determine the function between input and output. Thus, in order to
approximate a certain function, we need to find the best value for the weights. At the beginning, a loss function should be defined to measure the difference between the output value of the neural network and the true value. And then theoretically, weights can be acquired by solving

$$\frac{\partial \text{loss}}{\partial W} = 0.$$  

However, this equation is usually difficult if not impossible to solve analytically. Therefore, (stochastic) gradient descent is used to update the weights in practice. New values of weights are assigned in each update,

$$W \leftarrow W - \eta \frac{\partial \text{loss}}{\partial W},$$

where $\eta$ is the learning rate that determines the step size of updating. After a certain number of updates, a weight matrix that minimized the loss can be possibly obtained.

![Schematic architecture of a feedforward neural network with two hidden layers.](image)

**Figure 1-11** Schematic architecture of a feedforward neural network with two hidden layers. (b) The calculations of each node in the network and the analogy to the neuron in biological brain. (picture credit: Stanford CS231n website)

**b. Convolutional neural network (CNN)**

Although one can use feedforward neural network to perform an image recognition task, it is not a best approach since the positional relationships between
pixels would be ignored in this case. Convolutional layer, another type of hidden layers, is developed to address the problem. In a convolutional layer, there are a bunch of fix-sized image filters and each of them consists of weights for convolution. Each filter is applied to a partial area of the incoming image to get a convolved value, and by sliding over the whole incoming image, a new image can be obtained. This process is similar to applying filters in traditional image processing. The only different here is that instead of fixed weights for filters, the weights in convolutional layer are learned from task during training. Pooling layers are used to downsample the size of incoming image. Figure 1-12(a) illustrates the function of a 2x2 maxpooling layer, which is a simple select of the maximum value in the region of 2x2 pixels, which allows CNN to have positional invariant property. Figure 1-12(b) shows an example of CNN. In general, as the layer goes deeper and deeper, a larger number of filters and a smaller size of images are desired.
Figure 1-12 (a) Illustration of the functionality of a maxpooling layer. (picture credit: Stanford CS231n website) (b) A schematic example of the architecture of a convolutional neural network. (picture credit: WILDML website)
c. Recurrent neural network (RNN)

Unlike feedforward and convolutional neural network that take all the input data at once, recurrent neural network is the network that sequentially take part of the input data at different time step. Figure 1-13 shows the schematic of a recurrent cell and the illustration after unrolling it by time steps. For each time step of a temporal sequence data, RNN takes the input and interacts with its internal state of the cell to give an output. The internal state will pass to the next time step and do the same interaction until reaching the end. This special structure of RNNs makes them particularly suitable for tasks involving temporal sequence such as speech recognition. Nevertheless, the memories in a simple RNN hardly last more than a few time steps, which is problematic to long sequence data. LSTM is a cure for this [61]. It has gates for input, output as well as the transition of internal states between time steps. Controlling the gates makes the memory length more controllable in this case.

![Figure 1-13 Schematic of a recurrent neural network. (picture credit: colah's blog)](image)

1.4.2 Regression

Regression is a statistical process for estimating the relationships between independent and dependent variables. The estimation $Y$ of a regression,
\[ Y = WX + b, \]

is the expected value of a given input \( X \). \( b \) is the term to fix the biases. Generally, we would like to find \( W \) that minimize the mean square error (as the loss function) between the estimation and the target value (true value). This is known as the ordinary least squares regression. But by doing so we might overfit the training data and lose the generalization to unseen data. As a consequence, a penalty term of the weights is added to the loss function to regularize the model. A typical one is the L2 norm of the weights, which results into the following equation we would like to minimize.

\[
\min_W \|WX + b - Y_{true}\|_2^2 + \lambda \|W\|_2^2
\]

\( \lambda \) is the hyperparameter that determines the degrees of regularization. This is called ridge regression since it essentially equivalents to adding an additional fictitious data of the form

\[ x^f = (\sqrt{\lambda}, \ldots, \sqrt{\lambda}), y^f = 0, \]

which is like a ridge in the ordinary least squares regression. There are some other penalty forms for the weights, such as L1 norm (LASSO) or a combination of L1 and L2 norm (Elastic Net).

### 1.5 Summary

In this chapter, the thermodynamic origin of the self-assembling behavior of block copolymer and the subsequent pattern transfer methods to convert the BCP pattern into functional materials are described. The potential applications of BCP lithography in magnetic nanowires and nanodots are introduced, as well as the optimization method of the BCP pattern using machine learning and deep learning. In the following chapter of the thesis, the experimental methods that have been
used are firstly described (Chapter 2), and then the universal BCP pattern transfer methods are developed to dealing with different kinds of patterning requirements (Chapter 3). By using the methods, cobalt nanowires and Co/Pd, FePt nanowires with perpendicular anisotropy are fabricated to understand the domain configuration and interaction in the narrow nanowire arrays with small spacing (Chapter 4). CoFeB perpendicular MTJ nanopillar arrays are fabricated to understand the size-dependent switching behavior and the thermal stability after patterning (Chapter 5). Furthermore, the BCP lithography have also extended to 2-dimensional materials, in which we discussed the opto-electronic properties of MoS$_2$ monolayer after patterning as well as the potential mobility enhancement using corrugated gate dielectric (Chapter 6). Finally, we demonstrated using machine learning and deep learning algorithms to model the BCP self-assembly behavior, which allows us to improve the pattern quality by finding the optimal condition for solvent vapor annealing (Chapter 7). In conclusion, we demonstrated the pattern transfer methods that are applicable in most of the situation, explored and addressed the potential issue of high density, nanoscale magnetic structures that have not been studied before, and provided a new way to empirically model the BCP self-assembly behavior to improve the pattern quality in order to meet the industrial production requirements.


[34] X. Yang, S. Xiao, Y. Hsu, H. Wang, J. Hwu, P. Steiner, K. Wago, K. Lee & D. Kuo, Fabrication of Servo-Integrated Template for 1.5 Teradot/inch 2


CHAPTER 2
Research Methods

In this chapter, we describe the methods and tools that have been used in the research. Polystyrene-\textit{b}-polydimethylsiloxane (PS-\textit{b}-PDMS) block copolymers with different molecular weights are the main polymer we used in the experiments. Spin-coating and solvent-vapor annealing are used to form a BCP thin film on substrate and provide the environments for self-assembling process respectively. Methods in etching and pattern transfer are utilized to reveal the self-assembled BCP pattern and subsequently transfer the pattern into other functional materials. Vibrating sample magnetometer and alternating gradient magnetometer are used to measure the magnetic hysteresis of the patterned magnetic nanostructures. Magnetic force microscopy is used to image the magnetic configuration. OOMMF tool is used to simulate the domain wall behavior in patterned nanowires.

2.1 Polymers and Spin-coating

We have utilized several PS-\textit{b}-PDMS diblock copolymers with different molecular weights to generate the periodic pattern. PS$_{45}$-\textit{b}-PDMS$_{30}$, PS$_{37}$-\textit{b}-PDMS$_{16}$ were obtained from our collaborator, Prof. Avgeropoulos, in University of Ioannina. PS$_{47}$-\textit{b}-PDMS$_{9}$, PS$_{11}$-\textit{b}-PDMS$_{5}$ were purchased from Polymer Source Inc.
The as-synthesized PS-

b-PDMS are powders, so in order to form a thin film on our substrates, the BCPs are dissolved in cyclohexane (1wt\%) and then spun-coat, which is a procedure that uniformly spreads and deposits the material by spinning, onto the substrate. The BCP film thickness can be controlled by changing the rotation speed.

2.2 Solvent-vapor Annealing

In most of the cases, block copolymers (BCPs) themselves will not initiate the self-assembling behavior because the energy barrier for them to move around is too high. As a result, post annealing process is required for microphase separation. Thermal annealing and solvent-vapor annealing are the common two methods. In thermal annealing, heat is provided to the BCP films that allows the polymer chains to have a higher energy and potentially a largely increased diffusivity if the temperature is higher than glass transition temperature (T_g) of the majority polymer. Nevertheless, it might also cause the degradation of the polymer. On the other hand, solvent-vapor annealing is a proven powerful technique for allowing thin films of BCP to perform microphase separation and obtain the equilibrium structure [1–4]. In the process, a BCP thin film is placed in a chamber containing solvent vapor, and the thin film will absorb the solvent vapor and swelled to a higher film thickness, which actually creates the space and lowered the energy barrier for polymer chains to move around, allowing the self-assembly to happen. Figure 2-1 illustrates the solvent annealing process used in this thesis. The solvent is filled at the bottom of the glass apparatus with two outlets, where one is connected to a nitrogen flow and the other goes to the atmosphere. The solvent vapor pressure in the apparatus can be varied by different nitrogen flow rate which is controlled by a mass flow controller. Different solvent vapor pressure
will result in different swelled BCP film thickness, and as the swelled thickness is an important factor of the resulting morphology, it is monitored by spectral reflectometer throughout the annealing process. It is worth mentioning that the previous studies in our group have reported using co-solvent vapor for annealing, in exactly, toluene and heptane for PS-b-PDMS system, in which toluene would slightly prefer to swell the PS block and heptane is very selective to PDMS block. Thus, by controlling the ratio of toluene and heptane, we can possibly change the volume fraction of each block during the annealing and result into different morphology. Note that a dummy sample with the same condition as the experimental sample is used for in-situ film thickness measurement because the UV light from spectral reflectometer might have extra effects in the resulting morphology.

Figure 2-1 Schematic of solvent-vapor annealing process and setup. The graph on the top right corner shows an example of the thickness of a swelled BCP film over time.
2.3 Etching and Pattern Transfer

To reveal the morphology of BCP thin film and transfer the pattern into other functional materials, two kinds of plasma etching equipment were used in the thesis: the reactive-ion etching (RIE) and the ion-beam etch (ion-milling). Reactive-ion etching is a common dry etching process in microfabrication, which uses chemically reactive plasma to remove material deposited on wafers. The plasma is initiated in the system by applying a strong RF (radio frequency) electromagnetic field to the substrate holder. The oscillating electric field ionizes the gas molecules by stripping them of electrons, therefore create the plasma. As the chamber is grounded and the substrate holder is DC isolated, the electron deposited on the substrate holder will cause an accumulation of negative charges and thus build a large negative voltage on the holder, typically around a few hundred volts. The plasma itself develops a slightly positive charge due to the higher concentration of positive ions compared to free electrons. As a result of large voltage difference, the positive ions tend to drift toward the substrate holder, where they collide with the samples to be etched. The ions react chemically with the materials on the surface of the samples, but can also knock off some material by transferring some of their kinetic energy. Due to the mostly vertical delivery of reactive ions, reactive-ion etching can produce very anisotropic etch profiles. In our experiment, it is used to reveal the PS-b-PDMS BCP pattern, in which the PS block would be etched away by oxygen plasma while the PDMS block would turn into robust silica and left behind.

Unfortunately, the common gases in RIE, such as CF$_4$, CHF$_3$, O$_2$, SF$_6$, do not have chemical reactions with most transition metals and there is no volatile product to be formed, including the magnetic metals we interested in, Co, Ni, Fe, Gd, etc. As a result, instead of RIE, we use ion-beam etch to etch our magnetic
films. Ion-beam etch is a pure physical process that the high energetic ions are accelerated to bombard the substrate and mechanically eject the substrate material. Usually it works at the low pressure around $10^{-4}$ to $10^{-6}$ Torr since it need the ions to be ballistically transported. With this kind of etching mechanism, the ion-beam etch is highly anisotropic but has low selectivity to the etching species. With a mass spectrometer added to the ion-beam etch system, we can simultaneously analyze the ion species while doing the etching. As a result, we can in-situ monitor the etching profile and thus determine the end-point to finish the process.

2.4 Vibrating Sample Magnetometer (VSM)

Vibrating sample magnetometer is scientific instrument invented by Simon Foner at Lincoln Laboratory MIT that measures magnetic properties [5]. Figure 2-2 shows the schematic of VSM. In the instrument setup, the sample is placed in a uniform magnetic field generated by electromagnet to magnetize the sample, and then is physically vibrated sinusoidally. Therefore, there would be an induced voltage in the pickup coil which is proportional to the sample's magnetic moment, but does not depend on the strength of the applied magnetic field. The induced voltage is measured through the use of a lock-in amplifier using the vibration frequency as its reference signal. By measuring in the field of an external electromagnet at the same time, it is possible to obtain the magnetic hysteresis loop of a material.
2.5 Alternating Gradient Magnetometer (AGM)

In an alternating gradient magnetometer, the sample under study is magnetized by a uniform field created between electrical magnets poles, this causes the sample to generate its own magnetic field. Gradient coils produce alternating excitation field on the sample. The interaction between the sample’s own field and the excitation field displaces the sample alternatively left and right, proportionally to its magnetic moment. This displacement is measured by a piezoelectric sensor attached to the sample holder in a form of AC voltage. As a result, the magnetic moment of the sample under certain external field can be acquired. The measurement is operating at the frequency of a few hundred Hz, making the data acquisition much faster than VSM. The schematic of AGM is shown in figure 2-3.
2.6 Magnetic Force Microscopy (MFM)

Magnetic force microscopy is a secondary imaging mode of atomic force microscopy derived from tapping mode. It maps the magnetic force gradient above the sample surface while obtaining topographical data. In MFM measurements, the magnetic force between the sample and the tip can be expressed as

$$ F = \mu_0 (m \cdot \nabla)H, $$

where $m$ is the magnetic moment of the tip (approximated as a point dipole), $H$ is the magnetic stray field from the sample surface, and $\mu_0$ is the magnetic permeability of free space. The imaging relies on a two-pass technique, lift mode, in which the system alternates scan lines at the sample surface and at a designated
lift height above the sample surface, to separately measure topography and magnetic force, respectively. The typical spatial resolution is around 30 nm, and there are also some limitations of the MFM. For example, the recorded image depends on the type of the tip and magnetic coating, due to tip-sample interactions. The magnetic field of the tip and sample can change each other's magnetization, \( M \), which can result in nonlinear interactions and hinders image interpretation.

### 2.7 OOMMF

The Object Oriented MicroMagnetic Framework, OOMMF, is a project in the Applied and Computational Mathematics Division (ACMD) of ITL/NIST, in close cooperation with \( \mu \)MAG, aimed at developing portable, extensible public domain programs and tools for micromagnetics. The code is written in C++ and Tcl/Tk, including all the studied magnetic energies that may contribute to simulations. The energies included are exchange energy which is defined over pairs of spins, magnetostatic energy, anisotropy energy and Zeeman energy. With OOMMF, we can simulate the magnetism inside a material using as a premise that the magnetization can be viewed as produced by millions and millions of spins. The simulation is governed by Landau–Lifshitz–Gilbert equation.


CHAPTER 3
Universal Pattern Transfer Methods for Metal Nanostructures by Block Copolymer Lithography

This chapter is adapted from the previously published work in Nanotechnology [1].

3.1 Introduction

Arrays of metal nanostructures with dimensions of a few nm and above, produced from thin films, are essential components of electronic [2], photonic [3], optoelectronic, and magnetic [4] devices. Optical lithography lacks the resolution to pattern thin films into such small features, while the throughput of electron-beam lithography is limited, motivating the development of other forms of nanolithography. Block copolymer lithography is an attractive solution, characterized by high resolution and high throughput. In this process, thermodynamically-driven microphase separation of a block copolymer film generates ordered periodic microdomains with spherical, cylindrical or lamellar geometry. By removing one block and leaving the other, a nanoscale mask is produced which can be transferred into a functional material by etching or liftoff
processes [5], enabling applications in sensors [6], electronics [7–9], and superhydrophobic surfaces [10]. For diblock copolymers the morphology of the microdomains depends on the volume fractions of the two blocks, and the period of the microdomains depends on the degree of polymerization N, the Flory-Huggins interaction parameter χ, and the segment length. Design of the polymer chemistry and architecture therefore allows considerable control over the microdomain shape and size, with period ranging from a few nm to 100s of nm.

Pattern transfer is essential to convert block copolymer morphologies to functional materials. This can include processes where a material is precipitated directly within microdomains, such as the preloading of metal salts such as Au into polyvinylpyridine blocks followed by plasma etching [3], or sequential infiltration synthesis to introduce metal selectively into one block, such as tungsten into poly(methyl methacrylate) (PMMA) blocks [11]. These chemical processes have shown excellent results but offer limited filling factor, purity, and metal compositions.

Etching has been used to transfer microdomain patterns into many underlying materials, including multilayers or epitaxial structures. However, many transition metals cannot be easily etched by reactive ion etching. Ion beam etching may be used but this process typically exhibits redeposition and poor etch selectivity, requiring a hard mask. Cheng et al. used polystyrene-\textit{block}-polyferrocenyldimethylsilane (PS-\textit{b}-PFS), which has an iron-containing PFS block that converts to an iron and silicon oxide hard mask after oxygen plasma treatment, for patterning magnetic Co-alloy films [12]. Dot arrays were fabricated from CoCrPt films by using a PS-\textit{b}-PMMA block copolymer pattern to make a spin-on-glass mask for ion beam etching [13, 14]. Bit patterned media up to 1 T\text{dot}/in² was made using a nanoimprint template, which had a lower density of
features, to direct the self-assembly of PS-\textit{b}-PMMA, and then transferring the pattern to CoCrPt nanodots by imprinting and etching. The density was extended to 3.2 Tdot/in$^2$ by substituting PS-\textit{b}-PMMA with higher-$\chi$ polystyrene-\textit{b}-polydimethylsiloxane (PS-\textit{b}-PDMS) [15, 16].

Additive processes, in which a metal film is deposited on top or within the pores of a block copolymer mask, provide alternative routes. Jung et al. demonstrated transfer of grating patterns, rings and dot arrays into several metals including Ti, W, Pt, Co, Ni, Ta, Au and Al by a damascene-like process using PS-\textit{b}-PDMS [17], and a similar process was used to make NiFe nanodots using polystyrene-\textit{b}-polylactic acid (PS-\textit{b}-PLA) [18]. In this process a film was deposited over the block copolymer mask and planarized and etched back using a reactive ion etch. Lift-off processing has also been demonstrated in which the block copolymer is dissolved away after film deposition, leaving arrays of dots or lines at the locations of pores in the pattern [19, 20]. Other additive process such as electrodeposition have also been reported [21–25].

Each of these processes has been developed to pattern specific materials, and a detailed comparison of the capabilities of different pattern transfer processes has not been presented. This is particularly important for magnetic nanostructures where the magnetic reversal process and switching field is highly dependent on the shape, size and edge properties [12, 26–37]. Here, we demonstrate three different pattern processes, a Damascene-like process, a lift-off process and a subtractive process using ion beam etching, applied to the fabrication of arrays of cobalt dots and lines from the same PS-\textit{b}-PDMS block copolymer. Structural and magnetic comparisons of the cobalt nanostructures are reported in terms of uniformity, edge roughness and switching field distribution.
3.2 Experimental

A PS-\(b\)-PDMS diblock copolymer was selected for its high Flory-Huggins parameter \(\chi_{\text{PS-PDMS}} = 0.14 - 0.27\) at room temperature [39, 40]), which allows for scaling to sub-10 nm period and a sharp intermaterial dividing surface, and for the etch selectivity between the blocks and the etch resistance of the PDMS block [41-43]. On etching with an oxygen plasma, the silicon-containing PDMS block forms a silica-like material which can potentially be used as a hard mask. Furthermore, solvent vapor annealing has been demonstrated to provide tunable morphologies in the film, depending on the solvent vapor composition and vapor pressure [44-46]. The PS-\(b\)-PDMS used here (labeled as SD75) was synthesized and characterized as described in previous work [47]. The molecular weight was 75.5 kg mol\(^{-1}\), the polydispersity index was 1.04, and the volume fraction of PDMS \(f_{\text{PDMS}}\) was 0.415. In bulk, this material forms a gyroid structure with domain spacing \(d_{211} = 61\) nm and unit cell parameter of 150 nm [46].

To form ordered BCP thin films, silicon substrates were firstly modified with hydroxyl-terminated PDMS (3 kg mol\(^{-1}\), spin-coated then annealed at 170 °C, 12 hrs) in order to promote wetting. A 42 nm thick SD75 film was then spun-cast onto the PDMS-brushed silicon substrate from 1 wt% solution in cyclohexane, and solvent vapor annealed in a chamber 5 cm in diameter, 4.5 cm in height shown in figure 3-1(a). The chamber contained a solvent reservoir 4 cm\(^3\) in volume consisting of toluene and heptane with a volumetric ratio between 10:1 and 3:1. The toluene/heptane solution is non-ideal and the ratio of partial pressures of vapors differs from the ratio in the liquid [45]. A controlled flow rate of nitrogen of 2 - 5 sccm was flowed through the chamber by means of a mass flow controller. This provided control over the solvent vapor pressure and consequently the swelled thickness of the BCP film, which was monitored in situ by spectral reflectometry.
(Filmetrics, Inc., F20-UV, 250-1500 nm). In the toluene and heptane mixture, heptane vapor selectively swells the PDMS blocks and toluene can swell both blocks but becomes more preferential to PS as the heptane pressure increases [48]. By varying the solvent composition and partial vapor pressure during the annealing, the effective volume fraction of the blocks as well as the effective interaction parameter were changed, modifying the resulting equilibrium thin film morphologies [46]. In the annealing process, the BCP film was initially swelled to three times its initial thickness then deswelled to the desired swelling ratio by flowing nitrogen. After two hours annealing at the desired swelling ratio the film was dried by rapid exposure to air. The BCP films were then reactive-ion etched by a short 5 s of CF₄ to remove the PDMS surface layer (50 W, 15 mTorr, 10 sccm, in a Plasma-Therm 790) followed by 22 s of O₂ plasma (90 W, 6 mTorr, 10 sccm) to remove the PS and oxidize the PDMS microdomains, which were then imaged by SEM.

Depending on the solvent annealing conditions (Table 1), three morphologies were produced from SD75: hexagonally coordinated spheres (center-to-center spacing 69 nm ± 2 nm, row spacing 60 nm), in-plane cylinders (period 70 nm ± 3 nm, row spacing 61 nm) and perforated lamellae (period 92 nm ± 1 nm, row spacing 78 nm) shown in figure 3-1(b), 1(c), and 1(d). The perforated lamellae and in-plane cylinders were used for the pattern transfer processes described in this article. The initial thickness and swelling ratio of the BCP film, the effective χ parameter and the volume fraction, and the commensurability of the film thickness with the microdomain period all affect the final morphology. If the swelled thickness is incommensurate with the domain spacing, there is a greater tendency to form mixed structures or terraces rather than a uniform morphology [46].
After pattern transfer into Co, as described in detail below, samples were imaged by scanning electron microscopy with a resolution of 0.55 pixel nm$^{-1}$. Images were analyzed by the NIH public domain ImageJ software to obtain the average pattern dimensions of the morphology. To estimate the line edge roughness (LER) and the line width roughness (LWR), the SEM images were firstly converted to a binary map, the edge identified, and the LER and LWR obtained by calculating the 3-sigma value of the standard deviation. The magnetic hysteresis loops were measured by vibrating sample magnetometry in a field range of 10 kOe. Atomic force microscopy and magnetic force microscopy images were taken with a Dimension 3100 Nanoscope IV with a CoCr coated low magnetic moment tip.

Table 3-1 Solvent vapor annealing conditions for three different equilibrium morphologies of SD75.

<table>
<thead>
<tr>
<th></th>
<th>$N_2$ flow rate (sccm)</th>
<th>Solvent ratio (T:H)</th>
<th>Swelling Ratio (SR)</th>
<th>Annealing time (hr)</th>
<th>Temp. (°C)</th>
<th>Period (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spheres</td>
<td>2</td>
<td>10:1</td>
<td>2.3±0.1</td>
<td>2</td>
<td>25±1</td>
<td>69±2</td>
</tr>
<tr>
<td>Cylinders</td>
<td>5</td>
<td>5:1</td>
<td>1.5±0.1</td>
<td>2</td>
<td>25±1</td>
<td>70±3</td>
</tr>
<tr>
<td>Perforated lamellae</td>
<td>2</td>
<td>3:1</td>
<td>2.2±0.1</td>
<td>2</td>
<td>25±1</td>
<td>92±1</td>
</tr>
</tbody>
</table>
Figure 3-1 (a) Glass annealing chamber with nitrogen inlet and outlet to control the vapor pressure during solvent vapor annealing. The BCP film thickness is tracked by spectral reflectometry with the light transmitted through the quartz lid. (b)-(d) Representative SEM images of oxidized PDMS nanostructures formed from 42 nm thick SD75 thin films with different solvent annealing conditions listed in Table 1. T:H is toluene:heptane volumetric ratio and SR is swelling ratio.

3.3 Damascene Pattern Transfer Process

This process resembles a damascene pattern-transfer technique in which a metal, such as the Cu used in integrated circuit interconnects, is deposited over topographical features then etched back leaving only the metal within the trenches [49]. The process demonstrated earlier [17] was adapted for the SD75 features, and is schematically shown in figure 3-2. A 110-120 nm thick cobalt film was
conformally rf-sputtered on top of the oxidized-PDMS pattern (base pressure $= 5 \times 10^{-7}$ Torr, Ar flow rate $= 20$ sccm, Ar pressure $= 2.2$ mTorr, power $= 200$W, deposition rate $= 0.13$ nm/sec) and etched by a CF$_4$ reactive-ion etch (power $= 450$W, CF$_4$ flow rate $= 10$ sccm, pressure $= 10$ mTorr) for 30-40 minutes. The reactive-ion etch does not chemically etch the Co, but instead the Co was removed by physical bombardment by CF$_x$ ions which also planarized the cobalt film as sputtered material was redeposited within the valleys. When the buried oxidized-PDMS pattern was exposed to the plasma, it etched rapidly. Terminating the etch process at this point produced cobalt nanostructures with reverse contrast from the oxidized-PDMS, i.e. the perforated lamella structure produced a Co dot array.

![Figure 3-2 Schematic of Damascene-like pattern transfer process from BCP to metal nanostructures.](image)

Figure 3-3 shows the sample after different etch times, for samples made using (a) in-plane cylinders and (b) perforated lamellae. At 25 minutes, the films became smooth due to planarization, and at 30 minutes the Co was etched far enough to start to reveal the underlying oxidized-PDMS features. To determine the end point of etching, the film resistance was measured at each stage by a two-point measurement and an example is plotted in figure 3-4. The resistance increased slowly for times up to 35 minutes as the cobalt film was thinned by etching,
however, it rose dramatically at 38-40 minutes as the cobalt film became discontinuous, indicating the point at which the oxidized-PDMS was exposed.

Figure 3-3 Representative SEM images of cobalt films at different times during CF$_4$ reactive-ion etch. The sputtered cobalt film was planarized after 25 minutes etch. At 38 min the oxidized-PDMS had been fully removed and longer etch times caused shrinkage of the Co features. (a) cobalt nanowires transferred from a SD75 cylinder structure. (b) cobalt nanodots transferred from a SD75 perforated lamella structure.

Figure 3-4 Resistance of a cobalt film as a function of CF$_4$ reactive-ion etch time, measured with two-point probes placed 5 mm apart. It increased dramatically when the film was no longer continuous, indicating the completion of etching.
3.4 Lift-off process

Lift-off is commonly used for pattern transfer but requires soluble resist features with vertical or undercut sidewalls, and a collimated vapor deposition process such as evaporation to produce well-defined edge morphologies. The oxidized-PDMS features produced from spherical, cylindrical or perforated lamellar microdomains had a modest aspect ratio and evaporation of Co films did not lead to successful liftoff. Moreover, oxidized-PDMS is not soluble in organic solvents, requiring an HF solution which also degraded the metal film.

In order to enable liftoff, a PMMA layer was inserted as a sacrificial layer between the BCP and the substrate. PMMA is insoluble in cyclohexane, toluene, and heptane if it is crosslinked after baking, so that it is unaffected by the solvent annealing processes used for the PS-b-PDMS. Figure 3-5 shows a schematic illustration of the pattern transfer process. A 60 nm PMMA resist layer (950 PMMA, MicroChem, MW = 950 kg mol⁻¹, 1% in anisole) was spin-coated on a silicon substrate and baked at 180 °C for 90 s, followed by spin-coating 37 nm SD75 from cyclohexane and solvent vapor annealing as described above. Since the solubility parameter of PMMA is closer to PS than PDMS, it is expected that PS will wet the PMMA surface, unlike the silica substrates which have a PDMS wetting layer; therefore the PS-b-PDMS layer was thinner to ensure a commensurate film thickness. The thickness measurements were all carried out on a reference sample which had the same process parameter but without the PMMA layer underneath.

The annealed sample was reactive-ion etched for 5 s in CF₄ (50 W, 15 mTorr, 10 sccm) and an extended O₂ plasma time (90 W, 6 mTorr, 10 sccm) for 50 s, in order to remove the PS, oxidize the PDMS and to transfer the pattern
through the PMMA layer. Electron-beam evaporation was then used to deposit titanium (5 nm)/cobalt (20 nm) on top of the sample (base pressure = 7×10⁻⁷ Torr, deposition rate = 5 Å/sec). To carry out the lift-off, the sample was immersed into 80 °C NMP (N-methyl-2-pyrrolidone) solution (Remover 1165, MicroChem) for 1 hour, which dissolved the PMMA allowing the oxidized-PDMS/Ti/Co to float off. After rinsing with isopropyl alcohol and drying with a nitrogen gun, patterned Ti/Co nanostructures were obtained on the substrate.

As with the damascene-like process, the pattern was transferred with inverse contrast. Figure 3-6 shows images of cobalt nanodots and nanowires initially fabricated from perforated lamellar and cylindrical microdomain patterns respectively, which show the complete removal of the PMMA and overlying layers. The dots were on average 57 nm in diameter and 91 nm in pitch, whereas the nanowires were 27 nm wide and 64 nm in pitch. These dimensions were close to those of the original BCP patterns and are summarized in Table 2. A tapered edge (taper angle 35° ±5°) of the nanostructures was observed in cross section, which originates from the closing of the pores in the mask as metal is deposited. Continuing metal deposition would lead eventually to conical features, limiting the maximum height and aspect ratio of the structure. For example, for a taper angle of 35°, a particle with base diameter of 50 nm would be limited to a height of 36 nm.
3.5 Ion-beam Etch Process

a. Reverse contrast method

Etching of a pre-deposited film is the most general method for pattern transfer, enabling the patterning of multilayer stacks, epitaxial films, or films requiring high temperature growth or other conditions that would damage a liftoff
or damascene mask. Physical sputtering by ion-beam etching is used here, shown in figure 3-7.

Unlike the lift-off and damascene processes, the metallic films were deposited before the block copolymer mask. An evaporated 5 nm Ti/20 nm Co thin film was used for comparison with the lift-off samples. Oxidized PDMS itself can be used as a hard mask. Pattern transfer directly from oxidized-PDMS spheres from a 52 kg mol$^{-1}$ spherical-morphology PS-b-PDMS was attempted, but the ion beam etch resistance of the spheres limited the depth of Co that could be etched to a few nm.

Tungsten was instead chosen as a hard mask for its high resistance to ion beam etching [50, 51]. The lift-off process described above was used to obtain tungsten nanostructures on top of the film, either a dot pattern from perforated lamellar morphology or a line pattern from cylindrical morphology. After electron-beam evaporation and lift-off process, the tungsten mask obtained here was 25 nm thick with a $35^\circ\pm5^\circ$ taper angle, as shown in figure 3-8(b). An argon ion-beam was incident at a $55^\circ$ angle to the rotating sample to gradually mill away the uncovered cobalt film (Ar pressure = $2\times10^{-4}$ Torr, beam voltage = 450 V, accelerator voltage = 250 V). After 4 minutes etch, which was determined by the rising signal from titanium in an ion mass spectrometer endpoint detector (Hiden Analytical), the patterns were successfully transferred into the cobalt films.

Figure 3-8 shows the top view and cross-sectional images at different stages of the pattern transfer process, where (a), (b), and (c) show dot arrays and (d), (e), and (f) show line patterns. The left column (fig. 8(a), (d)) exhibit the transfer of the BCP patterns into PMMA. There was no collapse or distortion of the BCP/PMMA mask, which had an aspect ratio of about 2. The middle column (fig. 8(b), (e)), shows tapered tungsten nanodots and nanowires on top of the cobalt...
films after lift-off, which corresponds to step 5 of the process flow chart. The right
column (fig. 8(c), (f)) shows the etched cobalt nanodots and nanowires with the
residual tungsten mask. A taper is produced in the etched structures determined
by faster removal of the edges of the features compared to horizontal surfaces. The
taper angle was $25^\circ \pm 3^\circ$ for cobalt dots and $40^\circ \pm 5^\circ$ for the wires. The larger taper
angle of the cobalt nanowires is attributed to the faster erosion of the smaller width
masks. Detailed analysis of ion beam etching dynamics were reported elsewhere
[52, 53]. Table 2 lists the feature sizes estimated from the images at each step.
Because of the tapering introduced by etching, both the dot diameter and the line
widths were larger than those of the W pattern, while the period remained the
same.

Figure 3-7 Schematic of subtractive pattern transfer process from BCP self-
assembled mask by reverse transfer ion-beam etch process.
Figure 3-8 Plane view and cross-sectional SEM images at different stages during the ion-beam etch process. (a)-(c) show the transfer of a perforated lamellae pattern and (d)-(f) show the transfer of a cylinder pattern.

b. Direct transfer method

A direct transfer method, shown in the figure 3-9, was also developed to transfer the pattern from BCP into metallic film. Instead directly use BCP as the mask, which results into a limited pattern depth, carbon thin film is utilized here as it has a good etch resistance under ion-beam etch. First, a 20 nm thick carbon layer was sputtered onto the cobalt film at ambient temperature and then a PS-\textit{b}-PDMS layer was spin-coated on top of it. We have used PS-\textit{b}-PDMS with molecular weight of 56 kg mol\textsuperscript{-1} (PDMS volume fraction \textasciitilde16\%) (SD56) to generate a sphere pattern and PS-\textit{b}-PDMS with molecular weight of 53 kg mol\textsuperscript{-1} and 16 kg mol\textsuperscript{-1} to
generate cylinder patterns (PDMS volume fraction ~30%). After solvent vapor annealing, the same reactive ion etch process was used to produce an array of pillars and wires consisting of carbon with ox-PDMS caps (figure 3-10 (a)-(c)). Ion beam etching then produced an array of cobalt wires capped with C/ox-PDMS, as shown in figure 3-10 (d) and (e).

Figure 3-9 Schematic of direct transfer ion-beam etch process.

Figure 3-10 (a)-(c) Plane-view and cross-sectional SEM image of carbon hard mask. (a) Cylinder pattern. (b)(c) sphere pattern. (d)(e) The cobalt nanowire patterned with direct transfer ion-beam etch process.
3.6 Structural Properties of Transferred Pattern

Table 2 summarizes the line edge roughness (LER) of the nanowire patterns. LER is determined both by the roughness of the oxidized-PDMS patterns and by the fidelity of the pattern transfer steps. In a BCP, the width of the interface between the blocks is given by $t \approx \sqrt{2/3}a\chi^{-1/2}$, where $a$ is the Kuhn length of the segments. For PS-b-PDMS this is 1.46 nm taking $a = 6.7\text{Å}$ and conservatively $\chi = 0.14$. The interface width will provide a lower limit to the achievable edge roughness in the BCP patterns. The measured LER (3σ) of the oxidized-PDMS patterns on top of PMMA was 8.5 nm. This was reduced to 5.7 nm after transferring the pattern by liftoff into W or Co, suggesting the liftoff process smooths small scale edge variations. The subsequent ion-beam etch process from W into Co gave a similar LER of 6.1 nm, though the actual linewidth was larger. Line width roughness (LWR, 3σ) is another important metric, e.g. for interconnect fabrication since it affects the resistance of the wire. For uncorrelated edge roughness on each side of the line, $\text{LWR} = \sqrt{2}\text{LER}$, but in the microdomain cylinders the edges are expected to be correlated and the measured LWR was actually smaller than the LER, as low as 5.6 nm for the oxidized-PDMS. The LER increased to 7.3 nm for W lift-off features and 7.4 nm after ion-beam etch process, representing 15-22% of the linewidth.

For perforated lamellae, the average diameter and roundness of the holes in the BCP pattern as well as the W hard mask and Co dots after ion beam etching were calculated. The diameter showed little change (57.9 nm for the oxidized-PDMS holes, 57.2 nm after liftoff and 60.1 nm after ion-beam etch), with standard deviation (SD) of 3.0 nm for the oxidized-PDMS and 3.5 nm for the Co dots, as
shown in table 2. The average roundness (minor/major axis) at each stage was 0.89 – 0.93.

The preservation of the standard deviation of feature sizes and edge roughness throughout the pattern transfer process is encouraging for the application of block copolymer lithography. Further improvements in the uniformity of the initial BCP pattern may be anticipated by directed self-assembly using grapho- or chemo-epitaxy [54–65] which impose long-range order on the microdomain arrays, reducing the incidence of defects (e.g. 5- or 7-coordinated spheres in the case of close-packed dot arrays, or line terminations or junctions in the case of line arrays) which are associated with deviations in the size of microdomains.

Table 3-2 Structural characteristics at different stages during patterning. The values were obtained from image analysis of Figure 3-8.

<table>
<thead>
<tr>
<th></th>
<th>Cylinders</th>
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<th>Co wires (ion-beam etch)</th>
<th>Co wires (Damascene)</th>
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<th>BCP pattern</th>
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<th>Co dots (ion-beam etch)</th>
<th>Co dots (Damascene)</th>
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3.7 Magnetic Properties of Patterned Cobalt Nanodot Arrays

The magnetic hysteresis loops of Co nanodots fabricated by the three different pattern transfer processes are compared in Figure 3-11, with an unpatterned 20 nm evaporated cobalt film as a reference. The magnetic moment is
normalized to the sample area. The unpatterned cobalt films had a saturation moment of $2.71 \times 10^{-3}$ emu cm$^{-2}$, which corresponds to a saturation magnetization of $M_s = 1355 \pm 25$ emu cm$^{-3}$, which is similar to the bulk value for Co [32]. The low coercivity (25 Oe) and switching field distribution (SFD) are characteristic of reversal by the nucleation and propagation of domain walls within the film. The magnetic anisotropy is dominated by the shape of the sample since the polycrystalline film had no preferential crystallographic alignment. The out of plane loop was linear and did not saturate at 10 kOe as expected from the shape anisotropy field of 17 kOe.

For the Damascene-like process, the exact thickness of the Co nanostructures after etching is not known. Based on the area coverage of the dots, and assuming bulk $M_s$ of the Co, a thickness of 15 nm is predicted. However, inspection of the sample showed that up to half of the sample was covered by ~10 μm regions of Co which had not fully etched. This indicated a non-uniform etch rate across the film. The unpatterned regions are believed to account for the low coercivity of the sample.

The samples patterned by liftoff and ion beam etching showed lower magnetic moment per area and higher coercivity than the unpatterned film. The magnetic moment for the ion-beam etched dots was 25.8% of that of the unpatterned film, which is lower than expected from the areal coverage of dots of 36.8%. The lower moment is caused by the absence of dots in approximately 30% of the sample area. This arises from the presence of non-perforated lamellae or double-layer regions of the BCP film, which do not produce W dots after liftoff allowing the Co to be fully etched in those regions. For the Co dots made by liftoff, the saturation moment was 22.1% of that of the unpatterned film. Accounting for the tapered shape of the dots, this corresponds to 37% of empty area.
The cobalt nanodots patterned by lift-off and ion-beam etch processes had higher coercivity than the unpatterned film, 320 Oe and 177 Oe respectively. This is due to the different reversal mechanism, in which the dots behave as single-domain particles [32, 66] coupled by dipolar interactions. An isolated circular dot would have zero coercivity in plane, but the edge roughness and ellipticity lead to finite in-plane coercivity. For example, a Co ellipsoid with major axes of 20 nm, 60 nm and 54 nm (non-circularity = 0.9) would have a switching field of 491 Oe along its longest axis [67]. Variations in the shape, size and edge roughness lead to a switching field distribution, which may be exacerbated by magnetocrystalline anisotropy if the contributions of the grains do not average out over the limited volume of the dot.

Dipolar interactions between the closely-spaced dots also have an important effect on the reversal of the array. The interaction field between nearest neighbor dots was approximated by considering each dot as a magnetic dipole. By assuming a dot is magnetized in-plane in the +x direction and taking the dot radius as 30 nm and thickness as 20 nm, the x-component of its stray field at an angle of \( \alpha \) to the x-axis at a distance of 92 nm (the center-to-center distance of the hexagonal array) is +206.5 Oe, +129.1 Oe, -25.8 Oe, and -103.3 Oe for \( \alpha = 0^\circ, 30^\circ, 60^\circ \) and \( 90^\circ \) respectively. If all six nearest neighbors are magnetized in the same +x direction, a total field of +309.8 Oe will be present at the central dot. This stray field favors parallel alignment of the dots in the array, but as the field is reduced and dots start to reverse, the net field experienced by any given dot varies between \( \pm 310 \) Oe depending on the orientation of its neighbors. This leads to an increase in the switching field, additional to that produced from the shape, size and microstructural variation of the dots.
These two factors are believed to account for the SFD of the dot arrays. Notably, the SFD of the dots made by lift-off was much larger than that of the dots made by ion-beam etching. 90% of the magnetization reversed within a field range of 1800 Oe for the lift-off dots whereas the corresponding field range for the ion-beam etch process was 700 Oe. Since the nearest-neighbor interactions are expected to be similar, this difference is attributed to the greater structural variability of the lift-off process. Oxidation of the top surface of the lift-off dots may also play a role since the etched dots were protected by the W.

Localized topography and magnetic structure of ion beam etched cobalt nanodots and nanowires was probed by magnetic force microscopy (MFM) after DC demagnetization, as shown in figure 3-12. The imaging was done with a low moment tip, the lift height was 10 nm during MFM imaging and there was no filtering of the data. The MFM image of the etched cobalt dots (fig. 3-12(b)) shows a dark and bright contrast at each end of a diameter which is indicative of an in-plane dipole. The magnetization directions in most of the dots were parallel with their nearest neighbors, in agreement with the effect of magnetostatic interactions at remanence after in plane saturation. On the other hand, in the MFM image of cobalt wires, bright contrast was found either at the end of wires or at the location of large-angle bends, indicating the existence of magnetic poles and domain walls in the wires. The behavior of domain walls in nanowires will be discussed in more detail in the following chapter.
Figure 3-11 In plane hysteresis loops of cobalt nanodots patterned by three different processes compared to an unpatterned film.

Figure 3-12 The surface topography of ion beam patterned (a) cobalt nanodots and (c) nanowires imaged by scanning probe microscopy. (b)(d) The corresponding magnetic structure of the morphologies in (a) and (c).


3.8 Conclusion

This article demonstrates pattern transfer from a single block copolymer into Co thin films using three different routes: a Damascene process, a lift-off process, and an ion-beam etch process. Various pattern geometries were obtained by solvent-annealing the PS-b-PDMS BCP in different mixtures of toluene/heptane vapor. These processes produced reverse contrast, so that arrays of Co dots were produced from perforated lamellae, whereas in-plane cylinder patterns produced arrays of lines. Although not demonstrated here, spherical PDMS microdomains can be used to make antidot arrays by a damascene process [68]. Key to the liftoff and etch processes was the inclusion of a sacrificial PMMA layer under the BCP film, which increased both the aspect ratio and the solubility of the self-assembled pattern, allowing effective lift-off of the features. This could also be included in the damascene process if higher aspect ratio metal nanostructures were required.

Each of the three processes has its own advantages and limitations. The damascene process is well suited to patterning homogeneous films that could be deposited conformally. Liftoff requires non-conformal deposition such as evaporation, which limits the material compositions that can be produced, but it avoids the need for etching the material. Edge tapering from liftoff can affect the edge properties, particularly important for multilayer films. The ion beam etch process is the most universal and may be used to pattern epitaxial films, multilayer stacks or materials made under conditions that would degrade the mask, such as high temperature deposition. For example, patterning of magnetic tunnel junction stacks (not shown here) demonstrated that the ion beam etch process preserved the layer structure. Potential limitations of the ion-beam etching process include redeposition of the etched material, tapering and damage such as intermixing at the edges of the features, and the low aspect ratio of the features. Structural
analysis showed good fidelity during the ion beam etch pattern transfer in terms of line width, LER, dot diameter and its standard deviation. Additional chemical or topographical templating of the BCP can be implemented to produce arrays with long-range order and greater uniformity.

Magnetic characterization indicated significantly lower switching field distribution in the ion beam etched dot arrays compared with the array made by liftoff, which may be a result of a lesser influence of edge roughness. This study demonstrates the value of BCP patterning for making large areas of nanoscale magnetic structures for studies of switching, domain walls, and collective magnetic behavior.


[64] E. Huang, T. P. Russell, C. Harrison, P. M. Chaikin, R. a. Register, C. J.


CHAPTER 4

Magnetic Configuration and Interactions in 40 nm Wide Nanowires Made using BCP Lithography

4.1 Introduction

Magnetic nanowires have been studied both as model 2D magnetic systems and for applications in magnetic logic [1–3] and racetrack memory [4–8] devices. The understanding of the magnetic configurations of domain walls (DWs) in nanowires and their interactions as a function of geometry and magnetic properties is essential for developing DW-based devices [9–15]. There are many studies of DW structure [16–19], propagation [20–27], and pinning [8, 28–30] in nanowires; however, most of them are based on isolated wires with a width of ~100 nm or above, which is unfavorable in terms of developing high density, energy-efficient DW devices. Smaller-scale nanowires oriented out-of-plane with diameters a few nm and above have been synthesized within an oxide or polymeric matrix and their reversal process characterized [31–33]. In-plane nanowires with <20 nm linewidth have been made by planar processing with a block copolymer mask [34], but that work did not consider interactions between DWs.
DWs can adopt different configurations depending on the geometry and materials parameters of the magnetic system. For example, Bloch walls in bulk materials may be replaced by Néel walls in thin films as a result of the competition between demagnetizing energy and exchange energy. In thin film wires with in-plane magnetization, three types of DW configurations are commonly reported: transverse walls, asymmetric transverse walls, and vortex walls, depending on the ratio of the width/thickness of the wire and the exchange length of the material [24, 35]. A vortex wall (VW) which minimizes the stray field is favored in thicker and wider wires, whereas thinner and narrower wires favor a transverse wall (TW) which minimizes exchange energy, such as that shown in Fig. 2(a). An asymmetric transverse wall can be viewed as an intermediate state between a VW and a TW. In comparison, circular wires with small diameter are reported to have transverse walls and those with large diameter have a vortex-like curling wall structure [18]. The present article focusses on the regime of narrow nanowires in which the transverse wall dominates.

For wire arrays with easy axis along the wire, stray fields are only present at wire terminations or junctions and around DWs. The stray field distribution around a TW resembles a superposition of a monopolar field (i.e. a head-to-head DW produces a north monopole, a tail-to-tail configuration produces a south monopole) plus a dipolar field from the core of the DW in which the dipole lies transverse to the wire. Closely-spaced nanowires with DWs thus interact magnetostatically and there have been several computational and experimental studies of the effect of magnetostatic interactions between DWs in adjacent wires [36–44]. This includes interactions between VWs in closely-spaced half rings [37] or concentric rings [45]; the effect of interactions on the chirality of DWs [46]; and resonant excitation and correlated DW motion [38, 42, 47]. The experimental
studies were based on patterned thin film wires with widths on the order of 200 nm and larger or wires with large spacing between them, and there has not been an exploration of how interaction effects scale to smaller wire dimensions.

On the other hand, materials with perpendicular magnetic anisotropy (PMA) such as Co/Pd multilayers and $L1_0$-FePt stand out due to their high magnetocrystalline anisotropy ($K_u$) of $(1.6 - 70) \times 10^6$ erg cm$^{-3}$, [48, 49] which promises extremely high areal density of domain walls and high thermal stability of the magnetization [48–52]. Closely-spaced arrays of narrow wires with PMA provide model systems for studying not just the scaling of domain walls in wires but the effects of inter-nanowire interactions on the reversal behavior, which is a prerequisite for their applications in high density magnetic devices. However, studies of PMA nanowires arrays made of CoCrPt (linewidth $< 50$ nm), Co/Pt (linewidth $< 80$ nm), and Cu/Ni/Cu (linewidths $\geq 100$ nm) generally demonstrated the viability of electron beam, interference or block copolymer (BCP) lithography techniques in producing nanowires or analyzed anisotropy contributions to the wires. [53–56] Another study of PMA Co/Pt line arrays (linewidths and gap $\sim 200$ nm) illustrated Co/Pt magnetic configurations that were used for magnetic force microscopy (MFM) tip calibration. [57] Work on PMA Co/Pd multilayers and $L1_0$-FePt has investigated single nanowires, dot arrays and thin films. [58–61], but there are no examples of BCP-patterning of line arrays of PMA Co/Pd, $L1_0$-FePt and similar materials.

Block copolymer self-assembly can generate well-ordered structures with lengthscales of sub-10 nm to over 100 nm, providing a convenient tool to fabricate high density nanostructures over a large area [62, 63], reaching sizes below the resolution limit of optical lithography. For example, magnetic nanodot arrays have been made from cobalt [64, 65], CoPt [66], CoCrPt [53, 67, 68], Fe [69] and Co/Pd
multilayers [70], and various metallic nanowire arrays have been prepared, including magnetic nanowires of cobalt and nickel, but most of the work was focused on the pattern transfer process and the magnetic properties were not reported in depth [71–74].

In this work, a polystyrene-block-polydimethylsiloxane (PS-\textit{b}-PDMS) diblock copolymer was utilized to pattern dense cobalt nanowire arrays with wire widths of 40-50 nm, thickness of 20 nm and periodicity of 70 nm, and PMA [Co/Pd]15 and L10-FePt nanowires with 63 nm pitch length and 30-40 nm linewidth. The magnetic configuration of the arrays after demagnetization was imaged by magnetic force microscopy and analyzed using OOMMF micromagnetic simulations. In cobalt nanowire, we analyse both the magnetic structure and magnetostatic interactions of DWs in wires in a regime which reveals the interplay between the monopole and dipole components of the DW stray field. The results are relevant to the scaling of nanowire DW devices. In PMA nanowires, the magnetic hysteresis and the domain nucleation and expansion during reversal were studied.

4.2 Domain Wall Structure and Interactions in Cobalt Nanowires

4.2.1 Experimental

Titanium (5nm)/cobalt (20nm) thin films were prepared on as-purchased silicon substrates by electron-beam evaporation at a base pressure of $7 \times 10^{-7}$ torr and a deposition rate of $5 \text{Å sec}^{-1}$. A PS-\textit{b}-PDMS diblock copolymer with molecular weight of 75.5 kg mol$^{-1}$ was used to pattern the cobalt film into nanowire arrays by ion-beam etching. Details of the fabrication processes and structural characterization were reported previously [75]. Briefly, a sacrificial
polymethylmethacrylate (PMMA) layer was deposited on the cobalt layer followed by the PS-\(b\)-PDMS, and after solvent vapor annealing, the in-plane cylinder morphology of PS-\(b\)-PDMS was transferred into the PMMA layer by an oxygen reactive ion etch. A 20 nm tungsten film was then deposited onto the BCP/PMMA nanostructure using electron-beam evaporation. A liftoff process removed the PMMA to produce tungsten nanowires which were used as a hard mask during ion-beam etching to produce a dense array of cobalt nanowires. During AC demagnetization the applied field was oscillated between positive and negative values with 5\% decrease in amplitude at each cycle, starting from 10 kOe, whereas to obtain a DC remanence state a field of 10 kOe was applied for 10 seconds then reduced monotonically to zero. Surface topography and magnetostatic field configurations were imaged by atomic force microscopy (AFM) and magnetic force microscopy (MFM) respectively using a Dimension 3100 Nanoscope IV with CoCr-coated low moment tip. Micromagnetic simulations were carried out using the 3-dimensional OOMMF solver [76], in which the exchange constant was \(3 \times 10^{-7}\) erg cm\(^{-1}\), the saturation magnetization was 1400 emu cm\(^{-3}\), damping constant was 0.5, magnetocrystalline anisotropy was 0, and the cell size was 5 nm \(\times\) 5 nm \(\times\) 5 nm. There was no external field applied to the simulation environment unless specifically mentioned.

4.2.2 Results and Discussion

Figure 4-1(a) shows a plane view and tilted SEM images of a BCP-patterned cobalt nanowire array. The nanowires have a thickness of 20 nm, a line width of 50 ± 3 nm at the base and 20 ± 3 nm at the top, a 50\(^{\circ}\) ± 5\(^{\circ}\) taper angle of the edge, and a pitch of 70 ± 3 nm. Because of the lack of templating during block copolymer self-assembly, the nanowire arrays naturally formed a fingerprint-like
morphology without any preferred in-plane orientation, comprising locally parallel wires with bends of different angles as well as typical defects: Y-shape junctions, T-shape junctions, and wire terminations. Although nanowire arrays with long-range order can be obtained by directed self-assembly using chemo- or graphoepitaxy [77–79], we bypass this step in this experiment, since the untemplated patterns provide a variety of morphologies and wire angles with respect to the applied field.

To investigate the topography and corresponding magnetic structure in the nanowire arrays, the sample was firstly put into an AC-demagnetized or DC-remanent state using an in-plane field and then imaged by AFM/MFM to reveal the magnetization configurations at remanence. Figure 4-1(b), (c) show superpositions of the topographic image and the phase image which represents the stray field sensed by the tip after DC remanence [Fig. 4-1(b)] and AC demagnetization [Fig. 4-1(c)]. The phase signal is indicated with a red to blue color scale, representing magnetic field out of, or into the sample plane respectively.

At DC remanence, stray field is detected at terminations and junction points and at certain positions along curved sections of the wires. The latter contrast represents 180° DWs: head-to-head (HH) walls in red and tail-to-tail (TT) configurations in blue. A set of concentrically-curved wires is expected to form DWs of the same sense along a diameter parallel to the applied field, as seen in magnetic rings [40]. It is notable that walls of the same sense in adjacent wires appear to repel each other and move apart, behaving like monopoles confined in the nanowires, revealed for example in the boxed region of Figure 4-1(b).

After AC demagnetization, the magnetic domain walls are expected to have reached a low energy configuration within the energy landscape provided by the
wire geometry, pinning sites, stray fields and other inhomogeneities. Figure 4-1(c) shows the magnetization configuration of a sample after AC demagnetization. Wire terminations oriented in the same in-plane direction did not necessarily exhibit the same contrast, unlike the DC-remanent case. This indicates that the wires themselves are not all magnetized in the same direction. DWs in curved concentric sections were no longer of the same sense, and where HH and TT DWs were present in neighboring wires they were located in close proximity indicating attractive interactions, seen in the boxed region, analogous to the attractive interaction of DWs observed in 200 nm wide, 60 nm thick NiFe rings in Ref. 40.

Micromagnetic simulations were used to model the stray fields and interactions between DWs in narrow Co wires. A single nanowire with length of 1 μm, width of 40 nm and thickness of 20 nm containing a HH DW at its center was relaxed for 5 ns at zero field. The core magnetization of the DW was oriented along $y$, transverse to the wire, shown in Figure 4-2(a) indicating a transverse $180^\circ$ wall. This is consistent with previous reports that predicted the formation of TWs in thin narrow magnetic strips [35]. To mimic the field sensed by the MFM tip, we mapped out the $z$-component of the stray field in a plane 10 nm above the nanowire, shown in Figure 4-2(b). The out-of-plane field resembles the single contrast spot observed in the MFM images, confirming the monopole-like stray field measured above the DW. The oppositely oriented field from a TT DW is shown in figure 4-3.
Figure 4-1 (a) Scanning electron microscopy image of BCP patterned cobalt nanowire arrays, in which the dashed boxes indicate examples of typical defects including 1. Y-junction, 2. T-junction, and 3. line termination. Inset shows a tilted cross-sectional image of the wires. Cobalt nanowire arrays after (b) DC-remanence, and (c) AC-demagnetization. The magnetic force contrast was superposed on the topographic image for clarity. Red and blue show where stray field is present. DWs with the same sense repel, as shown in the dashed box of (b), while DWs with the opposite sense were attracted, as shown in the dashed box of (c).
Figure 4-2 (a) The magnetization of a head-to-head transverse domain wall in a cobalt nanowire simulated by OOMMF. Wire dimensions: 1000 nm long × 40 nm wide × 20 nm thick. (b) The z-component of the stray field produced by (a) in a plane 10 nm above the wire. (c) The y-component of the stray field in a plane at half the wire height. (d) Magnetic field amplitude of (c), which was acquired along the line through the center of the DW. (e) Enlarged section of (d) around y = 70 nm.
Figure 4-3 (a) The magnetization of a tail-to-tail DW in 40 nm wide cobalt nanowire. (b) The corresponding stray field in the z-direction in a plane 10 nm above the wire.

Additionally, the core of the TW contributes an in-plane dipole-like stray field. Figure 4-2(c) shows the field component in the y-direction, measured at half height of the wire. This is asymmetric on either side of the wire because on one side the dipole and monopole-like fields add and on the other side they subtract. The magnitude of the y-component of the field along the y-axis line through the center of the DW and at half the wire height is shown in figure 4-2(d), (e) for different wire thicknesses. On the +y side of the wire the field reached several kOe as the dipolar and monopolar fields added, but on the −y side the two fields oppose each other, resulting in a localized dipolar field at the edge of the DW surrounded by a broadly distributed monopolar field.

When considering interactions between a pair of DWs in adjacent wires, we can identify 16 possible cases because each of the DWs can be HH or TT and each can have its core magnetization oriented along +y or −y. Out of these, the six distinct cases are identified in Table 1 with letters A to F. Duplicate letters indicate
symmetry-related configurations in which the interactions are expected to be the same.

Table 4-1 List of 16 possible magnetic configurations of two transverse DWs in adjacent wires. The distinct cases are labeled A-F where in A, D : interactions depend on wire geometry, B : strong repulsion, C : strong attraction, E : weak repulsion, F : weak attraction. *schematic is provided in figure 4-4.

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<td></td>
<td>core ↓</td>
<td>D</td>
<td>C</td>
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Figure 4-4 Schematic of the magnetic configurations of two transverse DWs in adjacent wires. The uppercase letters correspond to the cases listed in Table 1.

Figure 4-5 shows the interactions between DWs in a pair of adjacent wires placed 30 nm apart, which imitated the geometry of BCP patterned samples, in two different cases. In case A of Table 1, the walls were both HH DWs with the same core orientation along +y. The walls repelled each other and moved apart.
(Fig. 4-5(a)), approaching the fixed boundaries at the ends of the wires within $t = 100$ ns. In contrast, in case C a TT DW and a HH DW, both with core magnetization along $+y$, did not move apart (Fig. 4-6(a)). To show that they experienced an attractive interaction, they were placed 500 nm apart, and they moved towards each other, reaching the center of the wire within 100 ns (Fig. 4-5(b)). Structures consisting of multiple parallel nanowires, longer wires, and wires with tapered edges showed similar results, which are detailed in figure 4-7 and 4-8.

![Figure 4-5 OOMMF simulations of DW interactions in two parallel wires. (a) two identical head-to-head DWs were initialized in the middle of the wire (case A in Table 1), and moved apart within 100 ns. (b) one tail-to-tail and one head-to-head DW (case C in Table 1) were initialized with an offset of 1000 nm, and the two DWs were attracted towards each other.](image-url)
Figure 4-6 (a) A tail-to-tail and a head-to-head DW (case “C” of Table 1) were initialized in the middle of two nanowires with the core magnetization aligned in the same direction. After 150 ns evolution the walls remained together at the same place. (b) Two identical head-to-head DWs (case “A” of Table 1) were initialized with a spacing of 10 nm, and stayed together after 150 ns relaxation.
Figure 4-7 The simulation of DW interactions in a multi-wire system. Wire dimensions were $2 \mu m \times 40 \text{ nm} \times 20 \text{ nm}$ (H), with periodicity 70 nm. (a) 2 wires, (b) 3 wires, (c) 4 wires, (d) 5 wires. The DWs have the same structure in each wire (case A of Table 1). In each case the DWs repelled each other and moved apart in opposite directions. When there was an odd number of wires, one of the wires stayed at the center of the nanowire.
Figure 4-8 Five nanowires were built with tapered edge with the cross-sectional image shown underneath. Head-to-head DWs were initialized in the middle of the wire, and after 100 ns evolution, they repelled each other, giving similar results as in figure 4-7(d).

Case B has two HH DWs with opposite core magnetization, and the interaction is strongly repulsive because both the monopolar field and the dipolar field from the core are repulsive. Case E is similar but the interactions are less repulsive: the dipolar field from the core is weaker because the low-field side of the dipoles are adjacent. These interactions remain repulsive for all values of stripe thickness, width and spacing that retain transverse walls. Analogously, the interaction of case C is highly attractive as seen in figure 4-5(b), and the interaction of case F is less attractive. The strength of the attractive interaction can be estimated by applying a field along the wire to separate the DWs. This required 455 Oe in C and 73 Oe in F (figure 4-9).

In cases A and D the high-field side of one DW and the low-field side of the other DW are facing each other. These situations can lead to either attractive or repulsive interactions depending on the geometry and spacing of the nanowires. As an example, case A showed a repulsive interaction for wire width of 40 nm,
thickness of 20 nm and spacing of 30 nm in figure 4-5(a). This agrees with our observation in DC-remanent samples. However, if the wire spacing is changed to 10 nm and thickness to 10 nm, the DW interaction is attractive (figure 4-6(b)). Figure 4-10 (a)-(d) illustrates how the DW interaction in case A varies as a function of wire width, wire thickness, and spacing between adjacent wires. All the simulations were initialized with both DWs placed in the middle of the wires and relaxed for 150 ns. For a wire width of 40 nm, shown in figure 4-10(a), there is an attractive interaction (Fig. 4-6(b)) for low thickness (< 10 nm) and narrow spacing (< 15 nm), otherwise, the interaction is repulsive. This can be understood by examining the field distributions along the y direction in figure 4-2(d,e). The field on the high-field side of the wire increased with wire thickness, since the monopolar field and the dipolar field were additive. On the contrary, the monopolar field and dipolar field were antiparallel on the low-field side, and because the monopolar field increased faster than the dipolar field when the wire thickness was increased, the total field became smaller immediately adjacent to the wire and changed sign closer to the wire. As a consequence, attraction occurred only when the two DWs were in close proximity and repulsion when they were further apart.
Figure 4-9 OOMMF simulation of DW behavior under an applied field in the $+x$ direction. (a) The initial magnetization of one HH DW in the top wire and one TT DW in the bottom wire, with their DW dipoles aligned in the $+y$ direction, corresponding to case “C” described in Table 1. (b) After applying a field in the $+x$ direction for 150 ns, the DWs could only be separated by a field larger than 455 Oe. (c) The initial magnetization of one HH DW in the top wire and one TT DW in the bottom wire, with their DW dipoles aligned in the $-y$ direction, corresponding to case “F”. (d) After applying a field in the $+x$ direction for 150 ns, the DWs could only be separated by a field larger than 73 Oe.
Figure 4-10 Mapping of the magnetostatic interactions between two identical DWs in parallel wires with width of (a) 40 nm (b) 80 nm (c) 120 nm (d) 160 nm as a function of wire spacing and thickness. The solid star in (a) shows the geometry of the actual sample. The repulsive behavior agrees with our experimental observation at DC-remanent state.

As the wires become wider, the range of wire spacings at which interactions are attractive decreases, and disappears at a wire width of 160 nm, as shown in figure 4-10(b)-(d). Rather than being caused by a change in the magnitude of the stray field, which did not change much with wire width, this phenomenon is attributed to the changing shape of the DW. As the wire width increases, the distribution of the positive charge (high field side) becomes much broader than the negative charge (low field side), and the DW shape becomes more trapezoidal,
figure 4-11. The extended dimensions of the DW therefore sample more of the extended monopolar field of the other DW. Additionally, the less rigid DWs in wider wires can be distorted by the stray field from the neighboring DW, which weakens the dipolar field and again promotes the dominant interaction with the monopolar field. Asymmetric TWs were observed when the wire was wide and thick enough (w > 120 nm, T > 20 nm), and although these DWs generally follow the trends of TWs, the interaction between them is beyond the scope of our discussion.

Figure 4-11 (a)-(c) The magnetization of head-to-head DWs in cobalt wires with different widths. Wire dimension: 2 μm (L) × (a) 40 nm, (b) 80 nm, (c) 160 nm (W) × 5 nm (H). The images shown here are not to the same scale. (d)-(f) the corresponding stray field in the y-direction of the DWs in (a)-(c) respectively.

Finally, we comment on the stray fields originating from nanowire junctions. Figure 4-12(a) shows an example of a T-shaped junction and figure 4-12(b) shows the corresponding MFM image after DC-demagnetization. An asymmetrical dark contrast was observed at the bottom left side of the junction. The T-shape junction was modeled with a wire width of 40 nm, thickness of 20 nm, and initial magnetization pointing to the right and upwards. After 10 ns relaxation, the configuration consisted of the lower wire magnetized to the right and the middle
wire magnetized upwards as shown in figure 4-12(c). The corresponding $z$-component of the stray field in a plane 10 nm above the wire is shown in figure 4-12(d), and qualitatively matches the MFM image of figure 4-12(b). Y-shaped junctions also existed in the BCP-patterned wire arrays, shown in the AFM [figure 4-12(e)] and MFM images [figure 4-12(f)]. Modeling of the magnetization and stray field was carried out, figure 4-12(g), (h), and the stray field gave a good agreement with the MFM.

Figure 4-12 Stray fields originating from nanowire junctions. (a)-(d) T-junction in a cobalt nanowire. (a) and (b) are the AFM and MFM images at DC-remanence respectively. In (b) an asymmetrical dark contrast was observed at the bottom left side of the junction. (c) the magnetization inside the T-junction simulated by OOMMF. The T-shape junction was modeled with a wire width of 40 nm, thickness of 20 nm, and initial magnetization pointing to the right and upwards. After 10 ns relaxation, the configuration consisted of the lower wire magnetized to the right and the middle wire magnetized upwards. (d) the corresponding stray field of (c) in the z-direction 10 nm above the wire, which qualitatively matches the MFM image of (b). (e)-(h) Y-junction in a cobalt nanowire. (e) and (f) are the AFM and MFM images respectively. (c) the magnetization inside the Y-junction simulated by OOMMF. (d) the corresponding stray field of (g) in the z-direction 10 nm above the wire. The stray field gave a good agreement with the MFM.
4.3 Domain Configurations in Nanowire Arrays with Perpendicular Magnetic Anisotropy

This section is adapt from the published collaboration work in Nanoscale [80]. Hopin did the thin film deposition, structural and magnetic analysis. I did the BCP patterning and HIM imaging. Congli did the TEM cross-section imaging. Jinshuo did the micromagnetic simulation.

4.3.1 Experimental

a. Co/Pd and L10-FePt Thin Film Deposition

[Co(0.6 nm)/Pd(1.2 nm)]15 was deposited at room temperature on Si substrates with native oxide by magnetron sputtering with Ar pressure of 10 mTorr and a base pressure better than 3 ×10⁻⁷ Torr. The Co and Pd deposition rates with deposition power of 25 W were 0.62 and 1.86 nm min⁻¹, respectively. FePt (20 nm) was ion beam sputtered on a (001) MgO substrate at room temperature from a Fe₅₅Pt₄₅ target, with Ar pressure of 1.5 ×10⁻⁴ Torr and base pressure better than 8 ×10⁻⁷ Torr. The FePt deposition rate was 0.033 nm s⁻¹ with an Ar ion gun discharge current, beam current and beam voltage of 0.9 A, 50 mA and 1000 V, respectively. The final composition of the sputtered FePt film was determined to be Fe₅₇Pt₄₃ from energy dispersive spectroscopy analysis. The PMA L1₀-FePt phase was subsequently formed from the as-grown disordered FePt by annealing at 700 °C for 2 hours under a base pressure of 9 ×10⁻⁷ Torr.

b. Block Copolymer Patterning

The [Co/Pd]₁₅ and L1₀-FePt thin films were then patterned using a self-assembled BCP film as am etch mask. A 20 nm thick carbon layer was first electron-beam evaporated on the samples using a power of 0.02 A, voltage of 10
kV, deposition pressure of $3.5 \times 10^{-5}$ mTorr and base pressure $2.2 \times 10^{-5}$ mTorr. The carbon layer provides a hard mask sufficient to protect the magnetic films during Ar ion-beam etching. A PS-\textit{b}-PDMS diblock copolymer with molecular weight of 75.5 kg mol$^{-1}$, polydispersity index of 1.04, and PDMS volume fraction of 0.415 was synthesized and characterized as described in previous work. [81] The PS-\textit{b}-PDMS BCP film (35 nm) was spin-cast on the [Co/Pd]$_{15}$ and $L1_0$-FePt thin films and solvent vapor annealed under flowing nitrogen (2-5 sccm) passing through a glass chamber of volume 88 cm$^3$ containing 4 cm$^3$ of toluene. After two hours of vapor annealing, the film was dried by rapid exposure to air. The BCP films were then reactive-ion etched for 5 s with CF$_4$ to remove the PDMS surface layer (50 W, 15 mTorr, 10 sccm, in a Plasma-Therm 790) followed by 60 s of O$_2$ plasma (90 W, 6 mTorr, 10 sccm) to remove the PS and oxidize the PDMS microdomains. The carbon under the PS was also removed, and the carbon/oxidised-PDMS patterns which were left behind acted as the hard mask. The combination of film thickness and annealing conditions produced a pattern consisting of a layer of cylindrical PDMS microdomains oriented in the plane of the substrate. The cylinders were locally parallel but their in-plane direction varied giving a fingerprint-like pattern.

The patterns were then transferred into the PMA Co/Pd and $L1_0$-FePt thin films by ion milling with an Ar-ion beam source of beam voltage 450 V, acceleration voltage 250 V, Ar pressure of $2 \times 10^{-4}$ Torr and base pressure of $9 \times 10^{-7}$ Torr. The ion milling process for Co/Pd was completed after 180 s when the Co profile from the secondary ion mass endpoint detector (Hiden Analytical) reached a plateau and the two-point probe resistance measurement of the film increased significantly from 120 $\Omega$ before etching to 1030 $\Omega$ after etching. The $L1_0$-FePt thin film required 200 s etch time before the Fe secondary ion mass profile plateaued and resistance of the film increased from 110 to 580 $\Omega$. 

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c. Structural and Magnetic Analysis:

The patterned features were imaged by a Zeiss ORION NanoFab helium-ion microscope (HIM). A focused ion beam (FIB, Zeiss Auriga) was used to prepare the samples for scanning transmission electron microscopy (STEM, FEI Titan) cross-sectional microstructure analysis. Magnetic properties of the PMA patterned and unpatterned films were characterized by an ADE model 1660 vibrating sample magnetometer (VSM). Lattice spacing and crystal orientation were studied using X-ray diffraction (XRD) on a Panalytical multipurpose diffractometer with Cu Kα radiation. Feature topography was measured using Veeco Nanoscope IV atomic force microscopy (AFM). The magnetic domain structures in the wires were mapped out with magnetic force microscopy (MFM, Veeco Nanoscope IV) using a CoCr coated low magnetic moment tip (Bruker MESP-LM). Simulations were performed with the three-dimensional OOMMF micromagnetic solver. Analysis of HIM and MFM images were carried out with the ImageJ processing program.

4.3.2 Results and Discussion

We first discuss the morphology and microstructure of the BCP-patterned [Co/Pd]₁₅ nanowires. Figure 4-13(a) shows an array of parallel cylinders of oxidized PDMS/carbon on a Co/Pd film, prior to metal etching, and Figure 4-13(c) shows the etched Co/Pd nanowires. Defects such as cylinder terminations and Y-junctions are visible in the BCP pattern. The Co/Pd nanowires had a pitch of 62 ± 3 nm, linewidth of 38 ± 4 nm and a spacing of 26 ± 3 nm. The measured edge root-mean-square roughness ($R_{RMS}$) of the BCP patterns and Co/Pd cylinders after pattern transfer were 1.5 nm and 1.0 nm, respectively, but this measurement is limited by the pixel resolution of the helium-ion microscope (HIM) images and the actual roughness may be lower. Figure 4-13(e) shows a scanning transmission
electron microscopy (STEM) cross-sectional image of the nanowires with a higher resolution inset illustrating a columnar polycrystalline structure. The wires had a width at the top of ~34 nm and spacing ~28 nm similar to the HIM images, but the cross-section reveals a wider footing at the bottom of the wires which extends about 10 nm out of the base of the wires, and a taper angle of 81° ± 4° at the sides of the wires. A slight etch into the Si substrate is also visible. The footings likely consist of redeposited material from the Co/Pd multilayer. Both Co/Pd unpatterned and patterned samples showed a (111) XRD peak [Figure 4-14], indicating a preferred texture.
Figure 4-13 Plane-view HIM images showing (a) BCP patterns on SiO₂/[Co/Pd]₁₅ and (b) BCP patterns on MgO/L₁₀-FePt. Inset of (b) shows a double layer BCP lamellar structure. (c) Co/Pd nanowires after pattern transfer. Inset of (c) shows a cross-sectional HIM image of the tapered Co/Pd nanowires. (d) L₁₀-FePt nanowires and other structures after pattern transfer. (e) Cross-sectional TEM image of BCP patterned Co/Pd nanowires. Inset shows the polycrystalline lattice of a Co/Pd nanowire, where the grain boundary is depicted by white symbols. (prepared by Congli)
Figure 4-14 XRD spectrum of (a) Co/Pd before and after BCP patterning (b) $L1_0$-FePt before and after BCP patterning. The unlabelled sharp peaks in (b) are inherent to the MgO substrate. (prepared by Hopin)
Next, we compare the magnetic properties of the [Co/Pd]_{15} before and after patterning. The magnetic moment per unit area decreased from $8.7 \times 10^{-4}$ emu cm$^{-2}$ (corresponding to saturation magnetization $M_s = 320$ emu cm$^{-3}$ for the unpatterned film) to $5.8 \times 10^{-4}$ emu cm$^{-2}$ after the removal of Co/Pd magnetic material not covered by the BCP mask. The change in magnetic moment per unit area suggests that 66 % of the Co/Pd thin film was left as nanowires, which is similar to the areal coverage of cylindrical features of 64 % determined from the HIM image [Figure 4-13(c)]. After patterning, the coercivity ($H_c$), anisotropy ($K_u$) and squareness ($S^*$) decreased significantly from $1990 \pm 50$ Oe to $790 \pm 50$ Oe, $1.64 \pm 0.20 \times 10^6$ erg cm$^{-3}$ to $0.97 \pm 0.14 \times 10^6$ erg cm$^{-3}$ and $0.97 \pm 0.23$ to $0.43 \pm 0.14$, respectively [Figure 4-15(a) and (b)]. The $K_u$ is estimated from

$$K_u = \frac{1}{2} M_s H_k,$$

where $M_s$ is the saturation magnetization and $H_k$ is the anisotropy field obtained from the extrapolation of the in-plane magnetization curve to saturation. The switching field distribution (SFD), determined as the full width at half maximum of the first derivative of the partial hysteresis loop $(dM/dH)$, also increased from $1700 \pm 50$ to $2440 \pm 50$ Oe. The tapering of the Co/Pd film and the distribution of wire sizes and shapes are assumed to lead to a spread in anisotropy and contribute to the SFD.

To clarify the effect of magnetostatic interactions, micromagnetic simulations were performed with the 3-D OOMMF micromagnetic solver to estimate the stray field distribution within a Co/Pd nanowire sandwiched by two neighboring Co/Pd nanowires and its effects on the Co/Pd DW dynamics [Figure 4-16(a)-(c)]. Each Co/Pd nanowire had dimensions of 40 nm wide $\times$ 4000 nm long $\times$ 27 nm thick, gap between neighboring nanowires of 25 nm, $M_s$ of 323 emu cm$^{-3}$,
uniaxial out-of-plane $K_u$ of $0.97 \times 10^6$ erg cm$^{-3}$ and exchange constant of $1.3 \times 10^{-6}$ erg cm$^{-1}$. The nanowire consisted of 6 layers of cells with cell size of $5 \text{ nm} \times 5 \text{ nm} \times 4.5 \text{ nm}$ to ensure simulation reliability. The damping constant was set to 0.1 for rapid convergence. The magnetic field at the centre and edge of the center nanowire due to the stray field from its two nearest neighbors magnetized in the same out-of-plane direction was 350 Oe and 516 Oe, respectively [Figure 4-16(a)].

By comparing the energies of relaxed Néel and Bloch walls in a single Co/Pd nanowire, a Néel wall was taken as the equilibrium structure with a 6.4 % lower energy [Figure 4-16(a)]. When a domain wall was introduced into the center nanowire, the stray field from the neighboring nanowires promoted DW motion leading to expansion of magnetization anti-parallel to that of the neighboring nanowires, figure 4-16(b,c), indicating the stray fields will produce antiparallel wire magnetization at remanence.
Figure 4-15 Hysteresis loop of (a) unpatterned SiO₂/[Co/Pd]₁₅ thin film, (b) BCP patterned array of Co/Pd nanowires, (c) unpatterned MgO/L₁₀-FePt (20 nm) thin film. Inset shows the XRD spectrum of the L₁₀-FePt before and after BCP patterning. The unlabelled sharp peaks originate from the MgO substrate. (d) BCP patterned array of L₁₀-FePt nanowires. (prepared by Hopin)
Figure 4-16 OOMMF simulations. In each case red and blue represent the component of magnetization out of the film plane and the arrows show magnetization vectors. (a) 3D schematic of a Co/Pd Néel DW and the magnitude of dipolar stray field experienced at the edge and centre of the Co/Pd nanowire from its two nearest neighbors. (b) Plan-view of three Co/Pd nanowires, with a Néel DW in the center nanowire, and the outer nanowires magnetized ‘up’ (red). (c) Propagation of the ‘down’ domain (blue) by Néel DW motion to the left in the center Co/Pd nanowire driven by the stray field from its neighbors. (d) 3D schematic of a \(L1_0\)-FePt Bloch DW and the magnitude of dipolar stray field experienced at the edge and centre of the \(L1_0\)-FePt nanowire from its two nearest neighbors. (e) Plan-view of three \(L1_0\)-FePt nanowires, with a Bloch DW in the center nanowire, and the outer nanowires magnetized ‘up’ (red). (f) Propagation of the ‘down’ domain (blue) by Bloch DW motion to the left in the center \(L1_0\)-FePt nanowire driven by the stray field from its neighbors. (prepared by Jinshuo)
The domains in a specific area of the Co/Pd nanowire array were imaged at remanence after AC demagnetization and after application of different reverse fields [Figure 4-17(a)-(e)]. Figure 4-18(a) shows the magnetic signal superimposed on the nanowire topography for the AFM and MFM data shown in Figure 4-17(a). Many of the wires showed magnetization direction opposite to their neighbors as expected from the stray field direction. By segmenting the $2 \times 2 \mu m^2$ region in Figure 4-18(a) into 100 portions of $0.2 \times 0.2 \mu m^2$ each, it was determined that approximately 75% of the neighbouring Co/Pd nanowires displayed opposite contrast after AC demagnetization. This can be seen in Figure 4-17(a) where the dark-light contrast in the MFM has double the period of the structure in the AFM, and the locations of DWs in neighboring wires are often adjacent to each other.

This indicates a preferential stable antiparallel magnetization configuration of the Co/Pd nanowires in the AC-demagnetized state as predicted from the micromagnetic simulation. Given the switching field distribution of Co/Pd nanowires (2440 Oe) and that the magnitude of the stray field just from the two closest neighbors (up to 516 Oe) is a large fraction of the $H_c$ of the Co/Pd nanowires (790 Oe), the demagnetizing field is large enough to produce an antiparallel configuration in many of the wires. The correlated domain patterns parallel to the wires are in stark contrast to the domain arrangements in the unpatterned Co/Pd film [Figure 4-17(f)]. The elongated domains in the Co/Pd nanowires had an average domain length of $460 \pm 20$ nm while the irregularly shaped domains in the unpatterned film had smaller average domain diameter of $270 \pm 20$ nm.

Even though most of the nanowires had antiparallel magnetization compared to their nearest neighbors, ~25 % of them displayed a parallel configuration. This is attributed to frustration when the nearest neighbors promote
opposite magnetization of the center wire, giving degenerate ground states susceptible to small perturbations. [83, 84]

To illustrate the reversal process of the array from saturation, the nanowires were first saturated with an out-of-plane field of $H_z = 12$ kOe giving a magnetization ‘down’ (yellow or light contrast) configuration. At a reverse field of $H_z = -500$ Oe [Figure 4-17(b)], reversed ‘up’ (red or dark contrast) domains with average size of $120 \pm 20$ nm nucleated in some of the nanowires. Specific reverse domains are identified (circled) so that changes in their geometry with increasing field can be seen. At an applied field of $H_z = -1000$ Oe [Figure 4-17(c)], the existing ‘up’ domains, with average domain size of $190 \pm 20$ nm, expanded slightly but the clearest effect is an increase in the density of ‘up’ domains. These observations suggest a limited domain wall mobility in the film such that domain nucleation occurs at lower fields than are required to translate the walls.

At $H_z = -1500$ Oe [Figure 4-17(d)], the reverse domains expanded along the wires, reaching an average size of $540 \pm 20$ nm. Many regions of adjacent wires (e.g. circled on the right of the image) showed antiparallel magnetization between neighbors as was seen in the AC-demagnetized sample. The stray fields combined with the applied field encouraged expansion of the ‘up’ domains along the Co/Pd nanowires as predicted in the micromagnetic model to produce the antiparallel magnetization state. At applied fields above $H_z = -2000$ Oe [Figure 4-17(e)], the ‘up’ domains further propagated leaving isolated ‘down’ domains stabilized by the stray fields.

A related behavior was seen in the unpatterned film where reverse domains formed at -500 Oe and further domains nucleated at -1500 Oe with little growth of the existing domains [Figure 4-17(g,h)]. Larger field led to expansion of the reverse
domains [Figure 4-17(i)-(j)] and at -4000 Oe only a few ‘down’ domains remained. The unpatterned and patterned films can be compared by plotting the fraction of reverse domains at remanence vs. field normalized to the saturation field, taken as 4.8 kOe for the unpatterned film and 3.2 kOe for the patterned film [Figure 4-18(c)]. For the initial stages of reversal, the patterned film had significantly more area fraction of reversed domains suggesting that domain nucleation was relatively easier in the nanowires, presumably facilitated at the edges of the wires, but for larger fields the reverse domains expanded proportionately more in the unpatterned film as they were unconstrained by the wire edges.
Figure 4-17 (a) AFM (left) and MFM (right) images of BCP patterned Co/Pd nanowires after AC demagnetization. (b-e) MFM images of Co/Pd nanowires at remanence after applying a field of $H_z = (b) -500$, (c) -1000, (d) -1500 and (e) -2000 Oe. (f) AFM (left) and MFM (right) images of unpatterned Co/Pd thin film after ac-demagnetization. (g-j) MFM images of unpatterned Co/Pd thin film at remanence after applying a field of $H_z = (g) -500$, (h) -1500, (i) -3000 and (j) -4000 Oe. All MFM images are captured at a fixed location on the patterned and unpatterned Co/Pd. Red and yellow contrast in the MFM images indicate ‘up’ and ‘down’ stray fields, respectively. (prepared by Hopin)
Figure 4-18 (a,b) 3D diagram showing the magnetic information (MFM) superimposed on the topography (AFM) of the ac-demagnetized (a) Co/Pd and (b) L1₀-FePt nanowires. Blue and red shading indicate ‘up’ and ‘down’ magnetization, respectively. (c,d) Area fraction of reversed domains versus applied reversed field as a percentage of saturation field for unpatterned and BCP patterned films of (c) Co/Pd and (d) L1₀-FePt. The dashed lines serve as a guide for the eye. The saturation field is taken to be the field at which the out-of-plane hysteresis loop closes. Saturation fields of the unpatterned Co/Pd, Co/Pd nanowires, unpatterned FePt film and FePt nanowires are 4.8, 3.2, 8.8, and 10.0 kOe, respectively. (prepared by Hopin)
We now describe the behavior of nanowire array made from a $L1_0$-FePt film. The BCP film on the $L1_0$-FePt thin film formed a less regular array of microdomains consisting of a mixture of cylinders, perforated lamellae [Figure 4-13(b)] and partially interconnected double layer lamellae [Figure 4-13(b) inset], compared to the BCP film on Co/Pd deposited and annealed under the same conditions. The BCP patterns on the $L1_0$-FePt had poor long-range ordering and larger rms line-edge roughness of 3.7 nm. The difference is believed to originate from variations in thickness of the BCP film on the $L1_0$-FePt thin film, which dramatically affects the BCP morphology.\textsuperscript{42} The $L1_0$-FePt thin film had a granular surface with high rms roughness of 2.9 ($\pm$ 0.5) nm (for comparison, the Co/Pd roughness was $\sim$ 0.8 $\pm$ 0.1 nm). In the regions of the $L1_0$-FePt film where nanowires had formed, their linewidth was 27 $\pm$ 8 nm, nanowire spacing was 30 $\pm$ 9 nm, centre-to-centre period was 63 $\pm$ 8 nm and measured rms edge roughness was 3.4 nm [Figure 4-13(d)].

The unpatterned $L1_0$-FePt thin film had an out-of-plane easy axis with $H_{c,OP}$ of 1.86 $\pm$ 0.05 kOe and an in-plane hysteresis loop with $H_{c,IP}$ of 1.12 $\pm$ 0.05 kOe [Figure 4-15(c)]. The XRD spectra of the unpatterned FePt thin film shows the FePt (001) superlattice peak and (002) fundamental peak [Figure 4-14], originating from ordering of the alternating Fe and Pt planes giving a (001)-textured fct $L1_0$-FePt. The extent of ordering is represented by the chemical ordering parameter,

$$S \propto \left(\frac{I_{001}}{I_{002}}\right)^{\frac{1}{2}},$$

where $I_{001}$ and $I_{002}$ are the integrated intensities of the (001) and (002) peaks. The unpatterned $L1_0$-FePt film gave $I_{001}/I_{002} = 0.45$ indicative of incomplete ordering of the Fe and Pt which is consistent with the in-plane hysteresis. The unpatterned

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film had $M_s = 644 \pm 30 \text{ emu cm}^{-3}$, $S^* = 0.50 \pm 0.14$, $K_u = 6.47 \pm 0.32 \times 10^6 \text{ erg cm}^{-3}$ and SFD = 7.81 ± 0.05 kOe.

Upon BCP pattern transfer onto the $L1_0$-FePt thin film, the magnetic moment per unit area decreased from 1.29 to $0.71 \times 10^{-3}$ emu cm$^{-2}$. This suggests that 55% of $L1_0$-FePt is left after patterning, which exceeds the estimated 46% areal coverage of cylindrical features calculated from the HIM image [Figure 4-13(d)]. This can be explained by morphological variations in the BCP, in particular regions of double layer cylinders which led to unpatterned areas of the film. There was a split of the (002) fundamental peak into two distinct (200) and (002) peaks after patterning [Figure 4-15(c) inset]. This suggests the presence of disordered A1-FePt phase formed from the sidewall redeposition of ion-milled materials during pattern transfer, which could also have contributed to the reduction of the nanowire anisotropy $K_u$ to $2.92 \pm 0.26 \times 10^6 \text{ erg cm}^{-3}$ [Figure 4-15(d)]. The $H_{c,OP}$, $H_{c,IP}$ and $S^*$ of the patterned nanowires also increased to 3.79 ± 0.05 kOe, 4.34 ± 0.05 kOe and 0.88 ± 0.18, respectively, presumably affected by the relatively large edge roughness, the inhomogeneity in the nanowire morphology and the crystal structure.

To examine the influence of dipolar stray field on the reversal process, OOMMF simulations were carried out on FePt nanowires with a dimension of 30 nm wide $\times$ 4000 nm long $\times$ 20 nm thick, a gap between adjacent nanowires of 30 nm, $M_s$ of 644 emu cm$^{-3}$, uniaxial out-of-plane $K_u$ of $2.92 \times 10^6 \text{ erg cm}^{-3}$, exchange constant of $1.3 \times 10^{-6} \text{ erg cm}^{-1}$ and damping constant of 0.1 [Figure 4-16(d)-(f)]. Each nanowire consisted of 4 layers of cells with cell size of 5 nm $\times$ 5 nm $\times$ 5 nm. The total dipolar stray field experienced by the center $L1_0$-FePt nanowire along its centre and edge was 445 and 583 Oe, respectively [Figure 4-16(d)]. Different from Co/Pd simulation results, both Néel and Bloch walls initiated in the $L1_0$-FePt
nanowire relaxed to give a Bloch wall [Figure 4-16(d)], which was taken as the energetically favourable DW structure for subsequent simulation [Figure 4-16(e) and (f)]. In the absence of an external field and omission of pinning from defects and edge roughness, the stray field emitted from the ‘up’ neighbouring nanowires encouraged the expansion of the spin ‘down’ domain and propagation of the Bloch wall to the left [Figure 4-16(f)].

Similar experimental protocols were used to examine the reversal of the $L1_0$-FePt nanowires as were used for the Co/Pd. A superimposed AFM-MFM image after AC-demagnetization [Figure 4-18(b)] shows that an estimated 40% of the nearest-neighbor $L1_0$-FePt nanowires were antiparallel to their neighbors, less than observed for the Co/Pd sample. OOMMF calculations indicated that dipolar stray field ($445 - 583$ Oe) from the neighbouring $L1_0$-FePt nanowires was much smaller than the coercivity $H_{c,OP}$ ($3.79$ kOe) and hence the stray fields are less effective in determining the magnetization state. The AC-demagnetized $L1_0$-FePt nanowire sample had an average domain size of $425 \pm 20$ nm [Figure 4-19(a)] which was similar to that of the uncorrelated labyrinth domain configurations in the unpatterned $L1_0$-FePt thin film with average domain size of $450 \pm 20$ nm [Figure 4-19(f)].

After saturation at $H_z = 12$ kOe, giving an initial ‘down’ configuration (yellow contrast), an applied field of $H_z = -2$ kOe [Figure 4-19(b)] led to nucleation of reverse ‘up’ domains (red) which expanded at larger reverse fields [Figure 4-19(c)-(e)]. There was no clear correlation of domains between adjacent wires, unlike in the Co/Pd sample. The reversal behaviour was similar to that of the unpatterned $L1_0$-FePt thin film [Figure 4-19(g) and Figure 4-20]. Furthermore, the area fraction of reversed domains vs. field was similar for the patterned and unpatterned $L1_0$-
FePt film [Figure 4-18(d)], suggesting that the reversal is dominated by intrinsic domain nucleation and growth rather than by the pattern geometry.

Figure 4-19 (a) AFM (left) and MFM (right) images of BCP patterned $L_1_0$-FePt nanowires after ac-demagnetization. MFM images with applied field of $H_z = (b) -2$, (c) -4, (d) -6, (e) -8 kOe, captured at a fixed location on the sample. MFM images of unpatterned $L_1_0$-FePt after (f) ac-demagnetization and (g) applied field of $H_z = -6$ kOe. Red and yellow contrast in the MFM images indicate ‘up’ and ‘down’ magnetization, respectively. (prepared by Hopin)
Figure 4-20 MFM images of unpatterned \( L1_0 \)-FePt (a) after ac-demagnetization and (b-d) at remanence after an applied field of \( H_z = \) (b) -2, (c) -4, and (d) -6 kOe. Red and yellow contrast in the MFM images indicate 'up' and 'down' magnetization, with the red domains favored by the negative applied field. (prepared by Hopin)

4.4 Conclusion

Large areas of closely spaced cobalt nanowire arrays with period of 70 nm, wire width of 40 nm, and thickness of 20 nm were fabricated by block copolymer patterning and imaged by MFM after AC- and DC-demagnetization. MFM contrast was found at the wire ends, junction regions, and at DWs. Micromagnetic simulations predict that the walls are transverse with their core magnetization oriented in the sample plane perpendicular to the wire. In terms of interactions the DWs behaved like monopoles, with walls of the same sense (e.g. both HH or both TT) in adjacent wires moving apart, whereas walls of opposite sense attract. This
behavior differs from that of wider or thinner regimes where the dipolar field from the DW core dominates magnetostatic interactions. Although the DW interactions in the wires of this study are dominated by the monopolar field, the dipolar field still plays an important role in determining the magnitude and symmetry of the stray field near the wire. DW interactions are predicted to be sensitive to wire geometry and spacing according to micromagnetic simulations, and the regimes of attractive and repulsive interaction were mapped out as a function of width, thickness and spacing for DWs of the same sense in adjacent wires. When the wires are thin and closely spaced, the dipolar field dominates and the DWs attract, but otherwise they repel. This work is relevant to understanding the potential crosstalk between DWs in densely packed nanowire racetrack devices, and the DWs could also serve as model monopoles in studies of interacting magnetic systems.

For PMA nanowire, [Co/Pd]_{15} and L1_0-FePt nanowire arrays with period 63 nm, linewidths of 27 – 38 nm, thickness of 20 – 27 nm and wire spacings of 26 – 30 nm were fabricated by ion beam etching using a carbon hard-mask patterned by a self-assembled PS-b-PDMS diblock copolymer mask, and the magnetic properties and reversal process were characterized. This process produced wires with a high aspect ratio (thickness/wire width = 0.71 – 0.74) with a predicted Néel domain wall structure in the Co/Pd and a Bloch wall in the FePt nanowires. In both cases dipolar stray fields from nearest neighbor wires are predicted to drive domain wall motion producing antiparallel magnetization directions in adjacent nanowires, but the ratio of stray field to coercivity is much higher for Co/Pd compared to FePt. Co/Pd nanowires showed a highly correlated domain structure in which adjacent wires had antiparallel magnetization and domain wall locations were aligned, as a result of the magnetostatic interactions. The study revealed domain nucleation was the dominant process at lower reverse fields with domain
wall propagation occurring at higher reverse fields, i.e. the nanowires exhibit limited domain wall mobility. The $L1_0$-FePt nanowires were less regular due to the effect of the higher film roughness on the BCP morphology, and the stray field was much smaller than the coercivity. This led to only a limited correlation between the magnetization directions of nearest neighbor nanowires.


CHAPTER 5
Magnetic Reversal and Thermal Stability of
BCP-patterned CoFeB Perpendicular
Magnetic Nanopillar Arrays

5.1 Introduction

Magnetic tunnel junctions with perpendicular magnetic anisotropy (p-MTJ) are of interest in memory and computing applications [1–3] because of their non-volatility and low critical current density for spin-transfer torque (STT) switching. These applications require high-density arrays of nanoscale MTJ devices in which good thermal stability, low switching field distribution and low interparticle interactions are desirable characteristics. These properties can be measured by magnetometry of large (mm-scale) area samples, but the limited resolution of photolithography and the limited throughput of electron beam lithography make these methods unsuitable for fabrication of such samples. Instead, a self-assembly method, block copolymer lithography, may be employed. Block copolymers can generate well-ordered periodic morphologies on the scale of over 100 nm to sub-10 nm [4–7], and transfer of the self-assembled patterns into magnetic films has been used to form arrays of magnetic wires and dots from a range of materials [8–14].
However, the behavior of p-MTJ nanoscale arrays made using this method has not been explored.

Perpendicular MTJs typically consist of ultra-thin CoFeB layers sandwiching an MgO tunnel barrier. PMA is produced by growth of the CoFeB on a heavy metal layer such as Pt or Ta, resulting in strong interfacial anisotropy, and the p-MTJs exhibit high tunneling magnetoresistance (TMR) (> 120%), low switching current, and high thermal stability. The growth [15–18], the physical origin of interfacial anisotropy [19], and voltage-controlled magnetic properties [20–22] have been extensively characterized. Scaling and switching behavior have been investigated in p-MTJ devices with diameters ranging from 11 nm to 500 nm [23–27], and the effective anisotropy was estimated by analyzing telegraph noise while measuring TMR using conductive atomic force microscopy [28]. These characterizations were done using electrical measurements on a few devices, and an ensemble analysis of their behavior is lacking.

In this article, a CoFeB/MgO/CoFeB p-MTJ was patterned into nanopillar arrays that cover a 0.5 cm × 0.5 cm sample area using block copolymer (BCP) lithography. Both direct and image reversal processes were developed to transfer the structure from the BCP to the p-MTJ stack forming p-MTJ nanopillar arrays with pillar diameters of 25 nm and 64 nm. Magnetic hysteresis measurements including first-order reversal curves [29] (FORCs) identified the switching behavior, switching volume and thermal stability as well as the magnetostatic interaction between the soft and hard magnetic layers in the p-MTJ nanopillars. By analyzing a series of hysteretic-dependent minor loops, FORC enables the irreversible switching processes to be identified as well as the corresponding coercive and interaction field in a range of magnetic systems [30, 31] that include multilayer thin films [32–34] and nanostructure arrays [35–38].
5.2 Experimental

MTJ stacks with the structure of Si/SiO₂/Ta(6)/Ru(10)/Ta(10)/
Co₂₀Fe₆₀B₂₀(0.8)/MgO(2)/Co₂₀Fe₆₀B₂₀(1.6)/Ta(7)/Ru(8) (thicknesses in nm), as
shown schematically in figure 5-1(a), were deposited at ambient temperature by
magnetron sputtering with a base pressure of 3 x 10⁻⁹ Torr. The sample sizes were
5 mm x 5 mm. The as-grown MTJ film then underwent a rapid thermal annealing
in Ar environment at 300 °C for 10 minutes to crystallize the amorphous CoFeB.
It was found the annealing step must be done before patterning since post-
annealing of patterned pillars led to degradation of the magnetic properties,
presumably due to oxidation or diffusion at the exposed edges of the pillars.

Two processes, the reverse contrast and direct transfer method that are
illustrated in figure 5-1(b) and (c) respectively, were used to pattern the annealed
p-MTJ film into nanopillar arrays. In the reverse contrast method, a 60 nm thick
polymethyl methacrylate (PMMA) resist layer (950 PMMA, MicroChem, MW =
950 kg mol⁻¹, 1% in anisole) was firstly spin-coated onto the p-MTJ film and baked
at 130 °C for 60 seconds, followed by spin-coating a 37 nm thick polystyrene-b-
polydimethylsiloxane (PS-b-PDMS) BCP with molecular weight of 75.5 kg mol⁻¹
and volume fraction ~41% PDMS (SD75) [6] (1 wt% in cyclohexane). The sample
then underwent 1 hour solvent vapor annealing in a glass chamber with 5 cm in
diameter, 4.5 cm in height [39], containing 4 cm³ annealing solvent of toluene and
heptane made from a 3:1 volumetric liquid mixture, which led to the BCP forming
a perforated lamellar morphology (Inset image of figure 5-2(a)) of the PDMS within
a PS matrix, with a PDMS wetting layer at the air surface. After the annealing, 5
s of CF₄ and 50 s of O₂ reactive ion etch were applied to the sample. The CF₄
removed the PDMS surface layer then the O₂ removed the PS, oxidized the PDMS
perforated lamella forming a silica-like material, and removed those areas of PMMA.
that were not protected by oxidized PDMS (ox-PDMS). The structure then consisted of a bilayer of ox-PDMS/PMMA containing close-packed pores with center to center spacing of 90 nm. A Pt hard mask was then deposited onto the sample via electron-beam evaporation (base pressure=7×10^{-7} Torr, deposition rate=5 Å s^{-1}) and liftoff (immersing in 80 °C NMP, n-methyl pyridine for 1h) was subsequently carried out to remove the PMMA/ox-PDMS/Pt, leaving an array of Pt dots on the MTJ film. Thus the PMMA is a sacrificial layer which enables the ox-PDMS to be removed by NMP, and also provides pores with nearly vertical sidewalls so that the Pt dot features formed at the base of the pores are well defined. The remaining Pt dots were used as a hard mask and the pattern was transferred into the p-MTJ stack by Ar ion-beam etching at 250 volts and 10 mA beam current. An endpoint detector was used during the etching process to keep track of the sputtered elements, and the etch was stopped immediately after the CoFeB/MgO/CoFeB layers had been etched. This process gives a contrast reversal from perforated lamellae of the BCP to nanopillar arrays of p-MTJ.

A direct transfer method, shown in figure 5-1(c), was also developed to transfer the pattern from a sphere-forming BCP into the p-MTJ film. First, a 20 nm thick carbon layer was sputtered onto the p-MTJ film at ambient temperature and then a 35 nm thick PS-b-PDMS layer was spin-coated on top of it, with molecular weight of 56 kg mol^{-1} and PDMS volume fraction of 16% (SD56) yielding a bulk morphology consisting of spheres of PDMS in a PS matrix. After solvent vapor annealing (15 minutes in toluene vapor environment), the same reactive ion etch process was used to produce an array of pillars consisting of carbon with ox-PDMS caps. Ion beam etching then produced an array of p-MTJ dots capped with C/ox-PDMS.
Figure 5-1 (a) A schematic of the layered structure of the perpendicular magnetic tunnel junction used in this work. (b)(c) Block copolymer patterning process for magnetic nanostructure. In (b) the perforated lamellar BCP pattern is transferred to the magnetic thin film with inverse contrast, while in (c) the sphere BCP pattern is transferred directly.

Although it is feasible in principle to produce nanopillars of both periods using the same pattern transfer method, practical issues need to be considered. One is that there is no commercially available sphere-forming BCP with high molecular weight, and even if there is, it is doubt the sphere pattern with large dot diameter is kinetically achievable. On the other hand, a perforated lamella forming SD36 was tried using reverse contrast method, but the structure was non-uniform on the PMMA underlayer. As a consequence, we used SD75 and SD56 which have strengths in perforated lamellae and sphere pattern respectively, and adopted the two processes for the patterning.

The patterned arrays were imaged by scanning electron microscopy (Zeiss Sigma) and the geometry was analyzed using the NIH public domain software ImageJ to calculate dot areas and densities. The magnetic hysteresis loops were
measured by alternating gradient magnetometry (Princeton MicroMag 2900) with the field sweep rate ranging from 4 Oe s\(^{-1}\) to 800 Oe s\(^{-1}\). Magnetic force microscopy images were taken by a Dimension 3100 Nanoscope IV atomic force microscope with a low moment CoCr magnetic probe.

5.3 Size-dependent Switching Behavior and The Effects of Magnetostatic Interactions

Figure 5-2(a) shows the SEM image after patterning the p-MTJ film from SD75 using the reverse contrast method. The resulting nanopillar arrays have a hexagonal close-packed structure with a periodicity of 90±2 nm. Assuming the nanopillars to be circular, the diameter distribution calculated from the areas of the dots is plotted in figure 5-2(b). The average diameter was 64 nm and the standard deviation was 4 nm, which is 6% of the diameter, showing good uniformity of the pattern. The result of the direct transfer method from SD56 is shown in figures 5-2(c) and (d). The periodicity is 38±1 nm and diameter is 25±2 nm, i.e. the standard deviation was 8% of the diameter.

Figure 3 shows the major magnetic hysteresis loops of the p-MTJ film measured before and after patterning, at a field sweep rate of 25 Oe s\(^{-1}\), measured from 5 mm wide samples. The unpatterned film, figure 5-3(a), exhibited PMA with a high remanence, square loop for an out-of-plane field. The upper CoFeB magnetic layer has higher moment and is expected to have a lower coercivity, but the hysteresis loop does not show two clear steps corresponding to separate switching fields. The coercivity was ~40 Oe and the saturation magnetization (\(M_s\)) was 492 emu cm\(^{-3}\).

The patterned MTJ nanopillars, figure 5-3(b), showed a lower moment per unit area of the substrate, a broader switching field distribution and higher

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coercivity for an out of plane field than the unpatterned film. The 64 nm diameter pillars (data shown in dark green) exhibited a two-step switching behavior, in which the softer layer switched at 150 Oe and the hard layer switched at 500 Oe, with each layer corresponding to about half of the total moment. The standard deviation of switching field distribution ($\sigma_{\text{SFD}}$) for the soft layer was 53 Oe and for hard layer was 166 Oe. In contrast, for the 25 nm diameter pillars, the switching field of the two magnetic layers were similar and no clear step was observed. The coercivity was 327 Oe and $\sigma_{\text{SFD}}$ was 199 Oe.

The saturation magnetization of the 25 nm pillars was about 35% of the value measured in the unpatterned film, which matches the areal coverage of the nanopillars of 37% based on the SEM images. However, for the 64 nm pillars, the saturation magnetization was actually lower than the areal coverage of 41%. This situation is caused by the absence of nanopillars in some of the sample area, where non-perforated lamellae or a double-layer morphology was formed by the BCP after solvent vapor annealing and thus there was no Pt hard mask left after liftoff.
Figure 5-2  (a)(c) Scanning electron microscope images of patterned p-MTJ nanoparticles. The inset in (a) shows the perforated lamellae BCP pattern used for inverse transfer method. (b)(d) The distribution of pillar diameters in (a) and (c) respectively.
Figure 5-3 (a) In-plane and out-of-plane hysteresis loop of unpatterned p-MTJ thin film, showing perpendicular magnetic anisotropy. (b) Out-of-plane hysteresis loops of p-MTJ nanopillars with diameter of 64 and 25 nm. The sample of 64 nm pillars showed a smaller magnetic moment because of the presence of regions without dots.

First order reversal curves, figure 5-4(a), were measured to further characterize the switching behavior of the patterned p-MTJs. For each curve, the measurement began with saturating the sample at 2 kOe, then the field was reduced to a reverse field \(H_r\), then the ascending loop was measured up to positive saturation. A series of curves was obtained with different \(H_r\). The step sizes of the field \(H\) and \(H_r\) were both 10 Oe.

We first propose which magnetization configurations correspond to various points on the FORCs for the sample with 64 nm diameter pillars, and show these schematically in figure 5-4(c). The light pink color represents up magnetization and the dark blue color represents down magnetization for the hard (lower) and soft (upper) layers. Points 1 – 5 correspond to the descending branch of the loop. At state 1, both layers of the p-MTJ nanopillars were magnetized in the up (positive) direction. When applying a reverse field, the soft layers switch over a field range of approximately \(H_r = 0\) to \(H_r = -250\) Oe, including states 2 and 3. If \(H_r\) is more
negative than -250 Oe, the hard layer in some of the pillars also switched, state 4, and when $H_r$ reached -800 Oe, both layers were magnetized down (state 5). Based on these configurations we consider the processes that occur while bringing the applied field from each of states 2, 3, 4 and 5 back to positive saturation. In the case of states 2 and 3, the ascending loop shows a step at around -120 Oe corresponding to the soft layers switching to the up direction. This suggests that the soft layers have an intrinsically low coercivity of below $\sim 30$ Oe since their coercivity from the midpoint of the descending branch was 150 Oe, and the offset from zero is due to the magnetostatic interaction from the hard layer, which will be calculated below. The ascending loop starting from state 4 showed additional steps, as it comprised two groups of pillars, group A in which both layers were magnetized down and group B with the soft layer magnetized down but the hard layer magnetized up. In the ascending loop, the soft layer of the pillars in group B switched to up at around -200 Oe, transitioning the sample from state 4 to state 6. As the applied field further increased, the pillars in group A begin to switch their soft layer to the up direction at around 150 Oe, state 7, followed at higher fields by the hard layer switching back to the up direction, regenerating state 1. The different switching fields of the soft layer in groups A and B is a result of the different directions of the magnetostatic field produced by the hard layer. Finally, the ascending loop starting from state 5 follows the opposite process of the descending loop from state 1 to state 5.
Figure 5-4 (a) First-order reversal curves of 64 nm p-MTJ pillars, showing only 1/10 of all the measured curves for clarity. (b) The corresponding FORC distribution. The color represents the value obtained from equation 1. (c) Schematics of the magnetic configuration of patterned nanopillar arrays. The numbers represent different configurations in (a).

Other than the steps in the hysteresis loop discussed above, we observe that the ascending loops exhibit an additional step at around 0 Oe. The magnitude of the magnetization change is approximately proportional to the fraction of the pillars that were in an antiparallel state as the field approached 0 Oe, i.e. greatest in the FORCs near the center of the major loop. We believe this step arises from magnetically soft material at the edges of the dots produced by damage from the ion-beam etching, which causes intermixing and disrupts the crystal structure. In this scenario, the largest low field step with magnitude $\sim 10\%$ of the net
magnetization change would correspond to a thickness of order 2 nm of low-anisotropy material around the edges of the dots.

Figure 5-4(b) plots the FORC distribution defined as

\[ \rho(H, H_r) = \frac{1}{2} \frac{\partial^2 M(H, H_r)}{\partial H \partial H_r}, \]  

where the axes are coercive field \( H_c = (H - H_r)/2 \) and interaction field \( H_u = (H + H_r)/2 \). The correspondence between figures 4(a) and 4(b) is shown by the colour coding. The purple peak at \( H_c = 100-200 \) Oe and the red peak at \( H_c = 300-350 \) Oe represent the switching of the soft layer for pillars in states A and B. The small red peak at \( H_c = 50 \) Oe and the purple peak at \( H_c = 350 \) Oe correspond to the reversal of the low anisotropy moment at the edge. Finally, the large green area at \( H_u \sim 0 \) Oe and \( H_c = 300-750 \) Oe is attributed to the hard layer switching. The two peaks that represent the soft layer switching have a difference in interaction field of \( \sim 150 \) Oe, meaning that the hard layer is exerting a field of \( \sim \pm 75 \) Oe on the soft layer. This is in agreement with our calculation of magnetostatic field in the later paragraph.

Figure 5-5 shows a series of magnetic force microscopy images of the p-MTJ pillars taken at remanence after applying different reverse fields. In (a)-(c), as the reverse field was less than 250 Oe, there were no obvious differences in contrast between pillars. This is consistent with the assumption that the anti-parallel state is not stable at remanence, i.e. any soft layers that were switched by the reverse field switched back at remanence due to the magnetostatic interaction from the hard layer. Figure 5-5 (d) and (e) show the images after applying -400 Oe and -500 Oe reverse field respectively. We start to see a clear contrast between pillars that are magnetized in the up direction and in the down direction, as in state 6 of figure.
5-4(c). As the reverse field increases, a larger fraction of pillars is switched to the down direction and all of them were magnetized down when the reverse field exceeded the saturation field (figure 5-5(f)). The uniform contrast within each dot supports the interpretation of single domain remanent states.

Figure 5-5 Magnetic force microscope images of 64 nm p-MTJ pillars. The field of view is 1μm x 1μm. (a)-(f) Images taken at remanence after saturating then applying different reverse fields. (d,e) show clear evidence of coexisting up and down net magnetic moment.
In contrast, the FORCs of the 25 nm nanopillars (Fig. 5-6(a)) did not show any clear steps when reversing the magnetization. Considering the magnetostatic interaction between the soft layer and hard layer, we believe the two layers switch together. However, a small kink was observed in the FORCs at an applied field of ~100 Oe, indicating two-step switching in at least some of the pillars. In the corresponding FORC distribution (Fig. 5-6(b)), the peak at $H_c = \sim 50$ Oe relates to the switching of the soft layer and the peak at $H_c = \sim 210$ Oe relates to the switching of the hard layer of those two-step switching pillars, while the ridge at $H_c = \sim 30$ Oe corresponds to pillars in which the two layers switched together.

Figure 5-6 (a) First-order reversal curves of 25 nm p-MTJ pillars, showing only 1/10 of the measured curves for clarity. (b) The corresponding FORC distribution of (a).

The magnetostatic interactions between the hard and soft layers is important in determining the reversal behavior of the p-MTJ nanopillars. Assuming the pillar forms a circular disk, we numerically calculate the field by integrating $H = \frac{q_m}{4\pi r^2}$ for both surfaces of the layer, where $q_m$ is the magnetic charge on the surface and $r$ is the distance from the charge to the target position. Figure 5-7(a) shows the out-of-plane component of the magnetostatic field originating from
the hard layer at the centerline of the soft layer as a function of radius. For 64 nm dots, the field varies from 60 Oe at the center to 135 Oe at the edge. Similarly the field produced by the soft layer at the position of the hard layer is plotted in figure 5-7(b), showing a higher magnitude. The magnetostatic field in plane away from the edge of the pillars is of opposite direction and decreases rapidly, with a value <10 Oe at the position of the nearest neighbor pillars. We therefore neglect interactions between neighboring pillars. Similarly, the vertical component of the stray field in 25 nm p-MTJ pillars is shown in red curve. Both the fields coming from the soft layer and the hard layer are larger in magnitude as compared to 64 nm pillars, leading to strong coupling between the two magnetic layers and accounting for the single-step reversal process. As the soft layer reverses, the interaction field exerted on the hard layer changes sign promoting to reversal of the hard layer.

Figure 5-7 Calculated out-of-plane magnetostatic field distribution of (a) the hard layer at the midline position of the soft layer and (b) the soft layer at the midline position of the hard layer.
We now consider the thermal stability of the p-MTJ pillars. Due to thermal instability, the switching field of small particles varies with the field sweep rate. From the Arrhenius–Néel formulation, the rate of magnetic reversal,

\[ r = f_0 \exp \left( -\Delta E/kT \right) \]

(2)

is defined by the probability per unit time of crossing the energy barrier \( \Delta E \). \( f_0 \) is the attempt frequency for barrier crossing and typically on the order of \( 10^9 \) s\(^{-1} \). \( k \) is Boltzmann’s constant and \( T \) is temperature in Kelvin. Assuming the Stoner-Wohlfarth (SW) model, the energy barrier can be written as

\[ \Delta E = KV(1 - H/H_o)^z, \]

(3)

where \( K \) is the magnetic anisotropy, \( V \) is the effective switching and \( H_0 \) is the field at which the energy barrier \( \Delta E \) is zero [40]. \( z \) is related to the direction of preferred axis and applied field, and according to an approximation made by Pfeiffer [41],

\[ z \approx 0.86 + 1.14x. \]

(4)

The \( x \) in equation 4 is the SW parameter determined by the angle \( \psi \) between the preferred axis and applied field, namely,

\[ x = \left[ \cos^{2/3}(\psi) + \sin^{2/3}(\psi) \right]^{-2/3}. \]

(5)

In addition, from the rate of magnetic reversal in equation 1, the magnetic moment of a collection of particles will decay exponentially in time \( t \) from a saturated moment \( m_0 \) under a constant opposing field, expressed as

\[ m(t) = m_0[2\exp(-rt) - 1]. \]

(6)
The relationship between coercivity $H_c$ and time $t$ can thus be derived,

$$H_c(t) = H_0\{1 - [(kT/KV) \ln(f_0 t)]^n\}, \quad (7)$$

using equations 1, 2, 5, $n = \frac{1}{z}$, and the definition of $H_c$ that half of the particles were reversed ($m(t) = 0$). To further correlate this to the field sweep rate, we take the derivative of $H_c$ with respect to $t$ and obtain

$$t = \frac{1}{R} nH_0[\ln (f_0 t)]^{n-1}(kT/KV)^n, \quad (8)$$

where the field sweep rate $R = -dH/dt$. Equations 6 and 7 can be fitted to experimental data to obtain $K$, $V$ and $H_0$.

The hysteresis loops of patterned p-MTJ nanopillar arrays under different field sweeping rate were measured by AGM and are plotted in figures 5-8(a) and 8(c). For 64 nm pillars, the coercivity of the soft layer did not show an obvious change with field sweep rate, but that of the hard layer increased from $481 \pm 5$ Oe to $692 \pm 8$ Oe as the field sweep rate increased from $4$ Oe s$^{-1}$ to $800$ Oe s$^{-1}$. It is important to point out here that the field shown in the hysteresis loops is the external applied field from the AGM, but to estimate the thermal stability characteristics, the actual field experienced by the sample population should be considered. This includes the magnetostatic field from adjacent layers and neighboring pillars in addition to the external applied field. Based on this, the actual coercivity of the hard layer changed from $631$ Oe at a field sweep rate of $4$ Oe s$^{-1}$ to $842$ Oe at $800$ Oe s$^{-1}$, taking into account the $150$ Oe magnetostatic field from the soft layer in addition to the external applied field. We then evaluate the thermal stability from the numerical solution of the effective time $t$ in equation 8, assuming $n = 0.614$ ($\psi = 10^\circ$), $H_0 = xH_k = 5000$ Oe and $KV/kT = 40$. The
coercivity and effective time $t$ were subsequently used in equation 6 to obtain a more accurate value of $KV/kT$ and $H_0$ by iterating between equations 7 and 8. Figure 5-8(b) shows the fitting of equation 6 and the results are listed in Table 5-1. The estimated thermal stability factor $(KV/kT)$ and anisotropy field $H_k$ were $43.5 \pm 1.1$ and $3305 \pm 99$ Oe respectively. At the same time, we also obtained $H_k$ by measuring the hard axis hysteresis loop (figure 5-9) of the patterned p-MTJs, yielding $\sim 5000$ Oe. The disagreement between measured and estimated value may come from the assumption of Stoner-Wohlfarth reversal or from the switching field distribution of the dots which leads to a range of thermal stability factors within the ensemble.

From $H_k = 2K/M_s$ and $M_s = 492$ emu cm$^{-3}$ from the unpatterned film, the magnetic anisotropy $K$ can be acquired, and the effective switching volume $V^* = 2.19 \times 10^3$ nm$^3$ at room temperature. The smaller $V^*$ compared to the actual volume of the hard layer ($r = 32$ nm, $h = 1.6$ nm, $\pi r^2 h = 2.57 \times 10^3$ nm$^3$) is consistent with the speculation of reduced anisotropy at the edges of the pillars.

The soft layer showed little scan rate dependence of its coercivity. The actual coercivity of the soft layer was estimated to be 10-70 Oe for different sweep rates after subtracting the magnetostatic field from the hard layer, which opposes the external field as the soft layers switch in the descending loop. The range of accessible sweep rates in the AGM was insufficient to yield a significant sweep rate dependent coercivity.
Figure 5-8 The hysteresis loops of (a) 64 nm and (c) 25 nm nanopillar arrays measured under different field sweeping rate. (b)(d) The linear fitting of the variation of coercivity with respect to log of the scan time $t$ (inversely proportional to the field sweep rate), from which the thermal stability factor and $H_0$ are obtained using eq. 8.
Figure 5-9 In-plane and out-of-plane hysteresis loops of (a) 64 nm pillar and (b) 25 nm pillar arrays.

Table 5-1 Estimation of the magnetic properties of BCP patterned p-MTJ nanopillars.

<table>
<thead>
<tr>
<th></th>
<th>Ku (erg/cm²)</th>
<th>V* (nm³)</th>
<th>Pillar V (nm³)</th>
<th>Hk (fitted) (Oe)</th>
<th>Thermal stability factor  Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>64 nm Hard Layer</td>
<td>8.15×10⁵</td>
<td>2.195×10³</td>
<td>2.574×10³</td>
<td>3305±99</td>
<td>43.5±1.1</td>
</tr>
<tr>
<td>25 nm</td>
<td>4.41×10⁵</td>
<td>2.520×10³</td>
<td>1.178×10³</td>
<td>1789±55</td>
<td>28.1±0.2</td>
</tr>
</tbody>
</table>

For the 25 nm pillars, since the hysteresis loops showed a single step switching behavior, we estimate the thermal stability by considering a pillar as a single magnetic dot. From table 1, the thermal stability factor was $KV^*/kT = 28.1 \pm 0.2$ and the magnetic anisotropy field $H_k = 1789 \pm 55$ Oe. It is hard to determine $H_k$ from the hard axis hysteresis loop (shown in figure 5-9(b)) as there is no obvious kink to make a reliable background subtraction. The effective switching volume was estimated as $2.62 \times 10^3$ nm³, which is larger than the volume of one pillar ($r = 12.5$ nm, $h = 2.4$ nm, $\pi r^2 h = 1.18 \times 10^3$ nm³). One potential reason for this is the smaller pillars are magnetostatically interacting with each other, which is possible since the spacing pillars is narrow. Nevertheless, the $H_k$ used here is acquired by
choosing the best fitting, which may not be representable since the measurement may be dominated by the pillars with strong response to thermal agitation and the real $H_k$ values may varies a lot and hard to be accessed.

The 64 nm diameter p-MTJ pillars therefore exhibit a field plateau within which the two layers are antiparallel, and a thermal stability factor $KV/kT$ of the hard layer exceeding 40. However, the 25 nm diameter pillars have lower thermal stability and the two layers do not switch independently due to the dominant effect of interlayer interaction. This can be improved by using a synthetic antiferromagnetic hard layer to reduce the magnetostatic field on the soft layer, or by increasing the PMA, e.g. by adding a Mo-dust layer between Ta and CoFeB [42].

5.4 Conclusion

In conclusion, CoFeB/MgO/CoFeB p-MTJ nanopillars with diameters of 64 nm and 25 nm were obtained using block copolymer patterning. Pattern transfer processes are developed to yield dot arrays from a perforated lamella or a sphere array, respectively, which include the use of a PMMA sacrificial layer to facilitate liftoff in the reverse contrast process, and a carbon hard mask for ion beam etching in the direct process. Magnetostatic interactions play an important role in coupling the hard and soft layers, especially for the smaller pillars. While the soft layer and hard layer in the 64 nm pillars reverse at different fields, the reversal of the two layers in the 25 nm pillars could not be distinguished. Hysteresis measurements suggest the presence of a magnetically soft component of the pillars which is attributed to ion beam damage at the edges of the dots. These results are relevant to the scaling of MTJ nanostructures for memory and logic devices.


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CHAPTER 6

Application of Block Copolymer Patterning for Two-Dimensional Materials

6.1 Introduction

Monolayer transition metal dichalcogenides (TMDs), such as MoS$_2$ and WS$_2$, are direct band gap semiconductors and offer new opportunities in electronics, opto-electronics and photonics beyond graphene [1–3]. A key aspect in realizing the potential of two-dimensional (2D) materials is the ability to create nanoscale structures with monolayer thickness, either by lithographically patterning a 2D film after growth, or by growing the 2D material directly as nanoscale dots or ribbons [4–6]. It is also important to understand how nanoscale patterning processing can change the electronic and optical properties of the 2D material. In graphene, nanoribbons have been synthesized by both approaches, with the latter accomplished by the high temperature reaction of molecular based precursors on a substrate [7, 8] and the unzipping of carbon nanotubes [9–12]. Chemical and solvothermal exfoliation of bulk MoS$_2$ has led to the production of small nanoparticles of MoS$_2$ with modified optical properties [13–17]. The recent advancements in chemical vapor deposition (CVD) growth of large-area 2D TMD
monolayer sheets offers an ideal platform for lithography and etching that will be compatible with electronic and opto-electronic device applications.

Patterning of 2D materials is often achieved using resist-based electron-beam [18, 19] and optical lithography methods [20], direct patterning by focused ion beams (Ga [21, 22] and He [23–25]), energetically preferred chemical etching [26, 27], nanoprobe cutting [28] and block copolymer (BCP) lithography [29]. Block copolymers, which consist of two or more incompatible blocks, microphase separate below their order-disorder temperature into periodic arrays of microdomains such as spheres, cylinders or lamellae [30–32]. Thin films of BCPs thus enable nanoscale patterning of various materials including silicon [33], silicon nitride [34], and metal oxides [35, 36] for use in air-gap structures, capacitors, field effect transistors, memories, and other devices [37]. In particular, BCPs have been used to pattern graphene into nanoribbons [29, 38, 39] with sub-10 nm widths for use in transistors, quantum dots [40], as well as hexagonal nanomesh [41]. Thin films of BCPs have been employed in templating the growth of 3D crystalline nanoparticles and nanowires of TMDs [42, 43]. To date there is little work on the direct patterning of 2D monolayer TMDs with BCPs to generate nano-structures and the comprehensive study of the impact this has on the direct band gap photoluminescence emission from monolayer TMDs such as MoS$_2$.

On the other hand, TMDs still limited by their low electrical mobility at ambient conditions. Efforts to improve the device performance through variety of routes, such as modification of contact metals [44] and gate dielectrics [44–50] or encapsulation in hexagonal boron-nitride [51], have yielded limited success at the room temperature.
Here, in the first part, we use BCP lithography combined with oxygen plasma etching to fabricate nanodots and nanorods in monolayer MoS$_2$ grown by CVD. A sacrificial polymethyl methacrylate (PMMA) layer between the MoS$_2$ and BCP enables the lift-off of the BCP etch mask after oxygen plasma etching, leaving behind bare MoS$_2$ nanodots and nanorods. The structures and properties of the MoS$_2$ film are investigated before and after the lift-off process. Characterization is performed using scanning electron microscopy (SEM), atomic force microscopy (AFM), Raman spectroscopy, and photoluminescence spectroscopy (PL), revealing a significant blue-shift of PL and stiffening of Raman modes attributed to the strain release in the monolayer domains through nano-patterning.

In the second part, we have demonstrated a large increase in performance of TMD field-effect transistors (FETs) operating at ambient conditions, achieved by using increased corrugation on substrate using BCP lithography. For MoS$_2$ transistors fabricated on crested substrates, we observed almost five-fold of magnitude increase in carrier mobility compared to standard devices on SiO$_2$ dielectric.

6.2 Experimental

a. Chemical vapor deposition growth of monolayer MoS$_2$

Molybdenum trioxide (MoO$_3$, ≥99.5%, Sigma-Aldrich) and sulfur (S, ≥99.5%, Sigma-Aldrich) powder were used to grow monolayer MoS$_2$ on a SiO$_2$/Si substrate (300 nm thick SiO$_2$) by chemical vapor deposition (CVD) at atmospheric pressure. Two furnaces were used to enable temperature control on both the precursors and the substrate. The heating temperatures for S, MoO$_3$ and SiO$_2$/Si substrate were ~180, ~300, and ~800 °C, respectively, with argon used as the carrier gas. To avoid cross-contamination between MoO$_3$ and S, MoO$_3$ powder was placed in an inner
tube having a smaller diameter, which was then inserted into the larger 1-inch quartz tube. The S powder was loaded in the outer quartz tube.

b. Block copolymer patterning and oxygen plasma etching process

On the substrate with CVD-grown monolayer MoS$_2$, a 30 nm thick PMMA (950 PMMA, MicroChem, MW = 950 kg mol$^{-1}$, 0.7% in anisole) was first spin-coated and then baked at 90 °C for 90 s, followed by spin-coating a 35 nm thick PS-$b$-PDMS film (Polymer Source, MW = 56 kg mol$^{-1}$, f$_{PDMS}$ = 16%, 1% in cyclohexane). Then the sample was put in a toluene vapor environment for the annealing process, which allowed the PS-$b$-PDMS to self-assemble into arrays of PDMS spherical microdomains. After annealing, 5 s of CF$_4$ (50 W) and 30 s of O$_2$ (90 W) reactive ion etch was applied onto the sample to oxidize PDMS dots (producing a silica-like material which resists O$_2$ plasma) and to remove the PS/PMMA/MoS$_2$ layers in the area that was not covered by the oxidized-PDMS.

c. Fabrication of surface corrugations on SiO$_2$ substrate

A 35 nm thick PS-$b$-PDMS film (Polymer Source, MW = 56 kg mol$^{-1}$, f$_{PDMS}$ = 16%, 1% in cyclohexane) was first spun-coat onto a thermally grown 300 nm SiO$_2$ substrate. The sample was then put in a toluene vapor environment for solvent vapor annealing for 15 minutes. After annealing, 5 s of CF$_4$ (50 W) and 30 s of O$_2$ (90 W) reactive ion etch was applied onto the sample to oxidize PDMS dots (producing a silica-like material which resists O$_2$ plasma), followed by a deep reactive ion etching (CHF$_3$ and Ar plasma for 10 s). The silica was further removed by HF etching.

d. Measurements

PL and Raman spectra were acquired using a Horiba LabRAM 800 HR spectrometer equipped with an Ar$^+$ (514.5 nm) excitation source and a Peltier-
cooled CCD detector. The laser was focused on the sample with a 400 nm confocal hole using the 100x objective under reflected illumination. The laser spot on the sample was \( \sim 1 \) \( \mu \)m in diameter and had a power of \( \sim 4 \) mW at the sample surface.

Scanning electron microscopy was performed using a Helios Nanolab 600 and a Zeiss Merlin, operated at 5 kV. Atomic force microscopy was performed using an Agilent 5500 scanning probe microscope in tapping-mode operation.

### 6.3 Nanopatterning of Photoluminescent MoS\(_2\) Monolayer

This section is a collaboration work with Grace Han and Prof. Jamie’s group in Oxford. MoS\(_2\) monolayer is grown by Prof. Jamie’s group. I have done the BCP nanopatterning and part of SEM imaging. Grace has done the other part of SEM imaging, AFM imaging as well as PL and Raman analysis.

MoS\(_2\) was grown using CVD, with triangular shaped domains on the scale of 10–100 \( \mu \)m randomly distributed across a 1 cm silicon wafer with 300 nm silicon oxide layer. A schematic illustration of the flow-chart process used to create the nanodots in MoS\(_2\) is presented in Figure 6-1a. PMMA is first spin-coated over the entire substrate to act as a sacrificial layer for lift-off in the final stages to remove any residual BCP. Next the substrate is coated with a polystyrene-\textit{block}-polydimethylsiloxane (PS-\textit{b}-PDMS) layer which self-assembles into periodic arrays of PDMS spheres embedded in a PS matrix through a toluene vapor annealing process, as previously reported [52–54]. PS-\textit{b}-PDMS is chosen for the fabrication of a self-organized nano-template because of its desirable etch selectivity, the formation of highly ordered features, and its scalability to small dimensions due to its high Flory-Huggins interaction parameter (\( \chi \)) [55]. Oxygen plasma is then used to preferentially etch through the PS region of the BCP and remove the underlying PMMA and MoS\(_2\). The exposure of PDMS to the oxygen plasma results in the
conversion to a silica-like oxidized PDMS (ox-PDMS) [56, 57] which is immobilized and selectivity covers the underlying PMMA layer and MoS$_2$. The remaining PMMA and ox-PDMS are then removed in a lift-off process by submerging the stack in acetone for at least 4 hours. Figure 6-1b and 6-1c show schematic illustrations of a nano-patterned MoS$_2$ monolayer domain composed of ~20 nm dots by the BCP-templated lithography.

Figure 6-1 Schematic illustration of the BCP patterning process for nanodot fabrication in MoS$_2$. a) Flow chart for nano-patterning procedure of monolayer MoS$_2$ domains using PS-$b$-PDMS block copolymers as an etch mask. Schematics of b) monolayer MoS$_2$ patterned in the shape of dots and c) an array of nanodots (~20 nm in diameter) formed as a result of BCP lithography.
The formation of nano-patterns before lift-off of the etch mask was confirmed by SEM as shown in figure 6-2. As-grown 10–100 μm MoS₂ domains with uniform contrast (Figure 6-2a) were covered first by a PMMA layer and then by a BCP film that generates hexagonally ordered spherical PDMS microdomains within a PS matrix, and a PDMS surface wetting layer, as previously reported [58]. After removing the PDMS wetting layer then etching the PS matrix in oxygen, the remaining oxidized PDMS microdomains serve as an etch mask, as seen in figure 6-2 b–d. Terracing happened during the annealing, as the BCP film thickness is not commensurate with the desired thickness of a monolayer of PDMS microdomain. While a monolayer region shows a dot array, the region with thicker BCP film would have a second layer of dots positioned on the gap of first layer dots, leading to a nanorod-like array after etching. Increased thickness of the BCP films produced a nanomesh pattern after etching and when too thick the MoS₂ was left unpatterned due to the lack of oxygen plasma penetration in the time interval used. The substrate is completely covered by the ox-PDMS pattern, displaying contrast between the areas covered either with rods (appear darker) or dots (lighter), which is clearly seen in figure 6-2d. The BCP is untemplated, and the pattern shows short-range order, with areas of rods and dots due to BCP thickness variations caused by terracing. Although not applied here, long range order can be imposed using topographical templates to guide the BCP self-assembly [59].

Figure 6-2e shows coexisting ox-PDMS dots and rods with brighter contrast relative to the substrate. The dimensions of the features were analyzed in figure 6-2f and 2g by measuring the line profiles of hexagonally ordered dots and parallel rods. The average diameter of the dots (20 nm) and the width of rods (16 nm) were determined by measuring the full width at half maximum of the line profiles. The average period of each pattern (35.5 nm for dots and 30 nm for rods) and varying
lengths of the rods (60–320 nm, commonly ~200 nm) were also measured by analyzing the SEM images.

Figure 6-2 SEM characterization of the nano-patterned MoS$_2$ fabricated by BCP and oxygen plasma etching. a) SEM image of the as-grown MoS$_2$ before BCP patterning. b) SEM image showing a large area of the sample covered with silica-like ox-PDMS nano-structures after oxygen plasma etching of BCP patterns. c) SEM image of a single triangular MoS$_2$ domain with ox-PDMS pattern. The dark micron-scale patterns represent the areas covered with ox-PDMS rods that are generated by the BCP bilayer. Lighter regions are covered with ox-PDMS dots that are formed by the BCP monolayer. d) SEM image with higher magnification showing the edges of MoS$_2$ domains (dark contrast) with the ox-PDMS mask covering the entire substrate. e) SEM image of the detailed structure of the ox-PDMS mask on MoS$_2$, showing the presence of well-ordered dot and rod arrays (light contrast). f) Magnified view of the region indicated with the red box in e) showing hexagonally packed ox-PDMS dots and the line profile of dots. g) Magnified view of the region indicated with the yellow box in e) showing ox-PDMS rods and their line profile. The average diameter or width of dots and rods is 16–20 nm.
Next we demonstrate that the nano-patterned monolayer TMDs can remain on the substrate after the removal of the lithographic mask. Acetone is used instead of NMP for the PMMA removal in order to prevent the detachment of TMD domains by the NMP. Figure 6-3a and 3b show the optical microscope images of CVD-grown pristine MoS$_2$ domains and those covered by the ox-PDMS after oxygen plasma etching, respectively. The bright micro-scale patterns in figure 6-3b consist of rods, and the rest of the substrate is instead covered with dots. After lifting off the PMMA sacrificial layer and the overlying ox-PDMS by immersing the substrate in acetone, we obtained mainly two types of MoS$_2$ domains as in figure 6-3c and 3d. The former exhibits mostly unvarying contrast within a domain, similar to a pristine monolayer, whereas the latter displays micro-scale patterns that resemble the arrangement of the ox-PDMS mask shown in figure 6-3b and figure 6-2c. The uniform domains were found near the edges of the substrate where the thicker spin-coated BCP film produced mainly rods and only a few dots. The domains in Figure 3d are present in the center of the substrate where a thinner BCP coating is formed and produces the mixture of ox-PDMS dots and rods after oxygen plasma etching. A SEM image of such domains (Figure 6-3e) exhibits both nanodots and nanorods of monolayer MoS$_2$, and the measured dimensions of the nano-patterns in figure 6-3f and 3g are consistent with those of the ox-PDMS structures in Figure 2. The uniform domains as in figure 6-3c are composed primarily of rod-shaped structures with a small number of nanodots interspersed as revealed by SEM (Figure 6-3h), similar to previously reported patterns formed with a PS-b-PDMS polymer [60]. The ratio of areas covered by dots and rods is determined by the thickness of the deposited BCP and affects the optical contrast of the nano-structured domains. The hexagonally ordered nanodots form continuous arrays in a large area up to 2 µm in width (Figures 6-3e and 3i), which
confirms the BCP lithographic method for creating nano-structured TMDs. Figure 6-4 and 6-5 show additional SEM images of MoS$_2$ at various scales from $\sim$100 nm to $\sim$10 $\mu$m that are patterned with nanodots, nanorods, and hexagonal nanomesh, depending on the thickness of the BCP film.
Figure 6-3 Optical microscope and SEM characterization of nano-structured MoS$_2$ after the lift-off process. Optical microscope images of monolayer MoS$_2$ domains that are a) pristine (as-grown), b) covered with an ox-PDMS mask layer, c) nano-patterned mostly with rods after the lift-off process, and d) nano-patterned with dots and rods. e) SEM image of a nano-patterned monolayer MoS$_2$ domain comprised of MoS$_2$ dots and rods, as the domain in d). f) Magnified view of the region indicated with the red box in e) showing hexagonally packed MoS$_2$ dots and the line profile of dots. g) Magnified view of the region indicated with the yellow box in e) showing MoS$_2$ rods and their line profile. MoS$_2$ is seen darker relative to the SiO$_2$ substrate. The average diameter or width of MoS$_2$ dots and rods is 16–20 nm. h) A domain patterned mainly in the shape of rods with smaller number of dots filling the space between rods, corresponding to the optical image c). i) Larger area of MoS$_2$ nanodot arrays with a hexagonal order. Bright dots represent ox-PDMS that remained after the lift-off process. (prepared by Grace Han)
Figure 6-4 SEM images of nano-patterned (a-c) micro- and (d) nano-scale MoS$_2$ domains in the form of nanodots and nanorods. Bright particles are residual oxidized PDMS dots that remained after the lift-off process. (prepared by Grace Han)
Figure 6-5 SEM images of nano-patterned (a-c) micro- and (d) nano-scale MoS$_2$ domains in the form of a hexagonal nanomesh. These domains are found near the edge of a substrate where thick layer of BCP is deposited. (prepared by Grace Han)

AFM topography in Figure 6-6 corroborates the results shown in figure 6-3. We probed nano-structured MoS$_2$ regions and ox-PDMS that was partially left behind after the lift-off process (Figure 6-6a). The center of the region was examined at higher magnification where coexisting nanodots and nanorods were found (Figure 6-6b). The height profile across the step edge of the MoS$_2$ domain on the substrate indicates a monolayer thickness (Figure 6-6c). The magnified regions from Figure 4b show the detailed structures of nanodots (Figure 6-6d) and nanorods (Figure 6-6e) that are well defined on the substrate. High-magnification topography of a region within Figure 4a is shown in figure 6-6f which illustrates
both dot- and rod-shaped MoS$_2$ structures, and their height profiles confirm they are a monolayer thick. Figure 6-7 contains additional AFM images of MoS$_2$ monolayers that are patterned with nanodots, nanorods, and hexagonal nanomesh, resulting from various thickness of BCP films.
Figure 6-6 AFM characterization of nano-structured MoS$_2$ after the lift-off process. 
a) Low-magnification AFM topography of nano-patterned monolayer MoS$_2$.  
b) Representative mid-magnification topography of the outlined area in a) (green) in the center of the MoS$_2$ domain.  
c) Height profile of the denoted section (blue line) in a) showing a monolayer thickness of MoS$_2$ on the SiO$_2$ substrate.  
d) Magnified view of the region indicated with the red box in b) showing nanodots.  
e) Magnified view of the region indicated with the yellow box in b) showing nanorods.  
f) Representative high-resolution topography of the outlined area in a) (white) near the edge of the MoS$_2$ domain, showing individual MoS$_2$ dots and rods. Height profiles from the respective red and yellow lines indicated in f) for g) nanodots and h) nanorods. The average height of ~1 nm corresponds to a monolayer thickness, and the average size of the nano-patterns of 16–20 nm matches the SEM characterization. (prepared by Grace Han)
Figure 6-7 AFM topography of (a) nano-scale domains patterned into dots and rods, (b-c) a micro-scale domain where dots are connected to form rods, and (d) a domain that is mainly patterned into nanomesh due to the thick BCP deposition. (prepared by Grace Han)

Optical properties of the nano-structured MoS$_2$ were investigated by photoluminescence (PL) spectroscopy on the selected spots of $\sim$1 $\mu$m size within MoS$_2$ domains. As-grown pristine MoS$_2$ domains and those covered by a PMMA layer exhibit identical PL spectra with a peak at 678 nm upon excitation at 514.5 nm (Figure 6-8a), suggesting a negligible effect of the PMMA coating on the photoluminescence of MoS$_2$ flakes. The parts within the domains covered with ox-PDMS dot etch masks show a blue-shifted PL at 663 nm and those with rods exhibit similar PL at 666 nm. The shift of 12–15 nm can be attributed to the release of the built-in strain in the monolayer MoS$_2$ that comes from the rapid cooling after
the CVD growth process [61], also supported by Raman spectroscopy measurements. Figure 6-8b shows the Raman spectra of pristine and nano-structured MoS$_2$ before the lift-off process. The $E^\text{1}_{2g}$ and $A^\text{1}_{1g}$ peaks correspond to in-plane and out-of-plane vibration modes [62]. The pristine MoS$_2$ shows characteristic peaks at 385 cm$^{-1}$ and 406 cm$^{-1}$ for $E^\text{1}_{2g}$ and $A^\text{1}_{1g}$ modes, and the spacing between these two peaks of 21 cm$^{-1}$ agrees with the frequency difference measured in high-quality monolayers as previously reported [63]. For the patterned monolayer, both characteristic vibration peaks are blue-shifted, by 1–2 cm$^{-1}$ for the $E^\text{1}_{2g}$ mode and 1–4 cm$^{-1}$ for the $A^\text{1}_{1g}$ mode, while the frequency difference between the two peaks decreases by 1 cm$^{-1}$ for nanorods but increases by 3 cm$^{-1}$ for nanodots. A similar degree of stiffening of the $E^\text{1}_{2g}$ mode has been reported for monolayer MoS$_2$ domains transferred onto other substrates (SiO$_2$/Si or h-BN) [64] through a two-step PMMA-assisted process that releases biaxial lattice tensile strain present in the MoS$_2$ domains directly grown on SiO$_2$. A further shift of $A^\text{1}_{1g}$ mode for nanodots, measured before the lift-off process in Figure 7b, is associated with their interaction with the PMMA layer and will be discussed in comparison to the Raman spectra of those after the lift-off in the next paragraphs.

After the lift-off of the PMMA layer and etch mask, the PL and Raman spectra of nano-structured MoS$_2$ were measured and compared to those of pristine domains. The degree of the blue-shift in PL of $\sim$15 nm resulting from the nanopatterning was similar to that seen before the lift-off process, indicating the marginal effect of a PMMA layer or an ox-PDMS mask on the PL measurement (Figure 6-8c). The stiffening of $E^\text{1}_{2g}$ and $A^\text{1}_{1g}$ modes by 1.5–2.5 cm$^{-1}$ and 0.5–1 cm$^{-1}$, respectively, was observed for respective dots and rods, similar to the blue-shift with nanorods before the lift-off (Figure 6-8b). As a control experiment, the PMMA-assisted transfer of MoS$_2$ pristine domains onto another SiO$_2$/Si substrate
was conducted, and $E_{2g}^1$ and $A_{1g}$ peaks at 387 cm$^{-1}$ and 406.5 cm$^{-1}$ were observed on the transferred MoS$_2$. The Raman shift of two modes overlaps with the other spectra measured from nano-structures after the lift-off, confirming the correlation between the release of strain and the Raman stiffening. Also, the relative intensity of the two modes ($A_{1g}/E_{2g}^1$) increases by a similar degree for the transferred pristine MoS$_2$ as for the nano-structured domains.
Figure 6-8 Optical property changes of MoS$_2$ domains induced by nano-patterning. Normalized photoluminescence (PL) a) and Raman b) spectra of monolayer MoS$_2$ nanodots and nanorods before the lift-off process (under an ox-PDMS mask after O$_2$ plasma etching) and those of pristine MoS$_2$ shown for comparison. Normalized PL c) and Raman d) spectra of monolayer MoS$_2$ nanodots and nanorods after the lift-off process and those of as-grown MoS$_2$ domains included for comparison. The Raman spectra of pristine domains transferred onto another SiO$_2$ substrate exhibits similar shifts of both E$_{2g}^1$ and A$_{1g}$ modes to those of nano-patterns. e) Relative PL of nano-patterned and pristine domains after the lift-off process (identical data as shown in c), normalized to the Raman A$_{1g}$ intensity. f) Plot of the relative PL as a function of the E/A ratio for the 4 different types of MoS$_2$. PL are all normalized to the Raman A$_{1g}$ peak. (prepared by Grace Han)

Since the stiffening of both E$_{2g}^1$ and A$_{1g}$ modes after the lift-off appears consistent regardless of the dimension of the MoS$_2$ domains, the more significant A$_{1g}$ blue-shift of the nanodots before the lift-off (Figure 6-8b) implies a doping level
change [65, 66] supposedly as a result of stronger interaction with the PMMA layer compared to that of other structures. The strong binding of nanodots to the PMMA layer and relatively loose attachment onto the SiO₂ substrate has been observed during longer lift-off processes where the nanodots were found detached from the substrate (Figure 6-9) as opposed to the remaining nanorod/mesh and to the pristine MoS₂ domains that were protected from O₂ plasma etching by a thicker PMMA coating.

The relative PL intensities of as-grown and nano-patterned MoS₂ domains are plotted by normalizing to the Raman A₁₈g mode intensity of each sample, which eliminates other factors from the comparison such as materials quantity, excitation intensity, and local electric field [2]. The Raman intensity and shift of the A₁₈g mode are reported to be more consistent compared to the E¹₂g mode with respect to varied density of sulfur vacancies [67]. Figure 6-7e shows that the PL efficiency of nanodots and nanorods is decreased to 13% and 42% of the pristine monolayer respectively, which is attributed to the increased defect trapping rate in the nanostructured domains carrying higher edge-to-area ratio. For the nanodots, the edge-to-area ratio (E/A = 4/diameter), is ~0.21 nm⁻¹ for the 18.7 nm dots. For the nanorods we measured typical E/A of 0.16 nm⁻¹, and for the nanomesh E/A of 0.055 nm⁻¹, which indicates that the nanodots have the highest edge density, followed by the nanorods and then nanomesh. Figure 6-7f plots the relative PL signal as a function of the E/A value for each MoS₂ region and shows a nonlinear trend of decreasing PL with increased edge density. This suggests that the reduction in PL efficiency is associated with increased edge effects. The edge region is presumed to have a higher degree of bond disorder than the crystalline interior due to missing nearest neighbor atoms and leads to lower exciton emission intensity as a result of increased quenching [68]. The PL spectra are all normalized to the
Raman $A_{1g}$ peak, which takes into account the different PL changes that would arise from the strain shift of absorption spectra. Time-resolved PL experiments were performed on pristine and nanorod MoS$_2$ domains, while the MoS$_2$ nanodots were difficult to measure accurately due to their lower relative PL intensity. The room temperature PL decay from the nanorods was nearly identical to the pristine domain with some convolution from the instrument response function (IRF), consistent with previous reports suggesting lifetimes $< 1$ ns [69, 70].

Figure 6-9 SEM images of nano-patterned MoS$_2$ domains with preferentially remaining nanorods and hexagonal mesh patterns after a long lift-off process (24 h in an acetone bath). Nanodots are loosely bound to the SiO$_2$ substrate and have a strong interaction with the PMMA layer, so they are lost after the lift-off. (a) A low magnification image of the etched triangular MoS$_2$ domains. (b) Magnified view of the nanorod/mesh region and mostly empty dot area. (c) Magnified view of nanorods and partially remaining dots between the rod patterns. (d) Nanorod/mesh patterns with partially empty spots that have lost nanodot flakes.
6.4 Enhanced Mobility in MoS$_2$ Field-effect Transistor with BCP Patterned Substrate

This is a collaboration work with Prof. Garaj’s group and his student Tao Liu and Liu Song in National University of Singapore. I did the BCP patterning of SiO$_2$ substrate. Tao and Liu did the field-effect electron mobility measurement.

As our collaborator has discovered the field-effect electron mobility can be enhanced by using high surface corrugations substrate as gate dielectric, shown in figure 6-10, it is important to have a method that constantly reproduces the desired surface corrugations with the periodicity of tens of nm. Electron-beam lithography is an option, but it suffers from low scalability and low processing speed. Therefore, BCP lithography was used here to create surface corrugations on SiO$_2$ substrates. After annealing and reactive ion etching, a hexagonal array of ox-PDMS dots with periodicity ~40 nm was obtained as an etching mask. Then a subsequent deep reactive ion etching and HF wet etching have resulted in a surface with roughness of $\delta z_{\text{RMS}} = 0.5$ nm (Figure 6-11a). Figure 6-11b shows the SEM image of the assembled polymer on SiO$_2$ surface forming regular patterns, together with the AFM image after etching and removal of the residual polymer. We fabricated 53 of the MoS$_2$ thin-film devices on the patterned surfaces, and measured their electrical characteristics under ambient condition. The mobility distribution for these devices is shown in figure 6-11c, with the average value of $\langle \mu \rangle_{\text{dot}} = 65$ cm$^2$V$^{-1}$s$^{-1}$, which is a factor of 5 improvement over the original performance of devices measured on a smooth SiO$_2$ substrates (Figure 6-12).
Figure 6-10 Substrate morphology dependence of MoS$_2$ FETs. a. Relationship between average FET mobility and substrate RMS roughness. The dielectric environment has no measurable effects on FET mobility. b. Statistical distribution of MoS$_2$ FET mobility on selected substrates. (prepared by Tao and Liu)

Figure 6-11 Pre-pattering method for improvement of FET performance on SiO$_2$ substrate. a. Schematic illustration of SiO$_2$ patterning using self-assemble polymer. b. SEM image of patterned etching mask and AFM image of resulted c-SiO$_2$ after etching. Scale bars are 250 nm. c. Distribution of MoS$_2$ mobilities measured for c-SiO$_2$ devices. (prepared by Tao and Liu)
The observed trend could be explained by the increasing effect of the strain field within the TMD sheets, originating from the surface morphology of the crested substrates. The tensile strain is predicted to decrease the bandgap and reduce the effective carrier mass, leading to increased electrical performance [71-73] and carrier mobility [74]. Previously, scanning-tunnelling experiment [75] showed that even moderate substrate’s roughness could induce sufficient strain to significantly modify the local bandgap in monolayer MoS$_2$; and fluctuations in the optical band gap has been observed for MoSe$_2$ deposited on the rough substrates [76]. The Raman spectra measured for MoS$_2$ sheets on crested surfaces showed softening of the in-plane E$_{2g}^1$ mode and increase in the linewidth (Figure 6-13), compared to flat surfaces. This is consistent with the strain effects [61, 62, 77], averaged over a non-uniform strain field.
Figure 6-13 Raman spectra of MoS$_2$ on SiO$_2$ and c-SiN$_x$ substrates. Both samples have same thickness. Peak softening is observed for c-SiN$_x$ supported sample. (prepared by Tao and Liu)

### 6.5 Conclusion

We have demonstrated the potential of incorporating BCP lithography with 2D materials. The use of BCP lithography has enabled the fabrication of nanodots, nanorod and nanomesh features in monolayer MoS$_2$. The patterning was successful across large scale areas up to 1cm x 1cm, and uniform areas of nanodots as large as 2 μm were achieved. The ability to produce micron-scale uniform areas of nanodots, nanorods, and nanomesh enabled their separate probing by photoluminescence and Raman spectroscopy, revealing reduced PL efficiency in nanodots compared to nanorods and nanomesh, which we attribute to increased edge density. Even though nanorods with widths down to 4 nm were present in the samples, no evidence for quantum confinement effect was found, nor in the nanodots that are ~19 nm. This is expected since the Bohr radius of a monolayer MoS$_2$ exciton is calculated to be 0.5–1 nm [78–80], which requires the lateral size reduction of nanodots down to the 1–2 nm scale in order to observe any quantum confinement effect across the 2D plane [16]. These results show that increased edge density causes decreased PL efficiency and that the BCP lithography process
results in the release of strain that forms during the CVD growth and cooling process. However, the confirmation that small 19 nm nanodots of MoS2 still exhibit strong PL is promising for their future implementation in photonic based nanoscale applications. Further work to improve the PL efficiency may involve the functionalization of the edges to reduce quenching in order to enhance their potential impact in future photonic and opto-electronic applications.

Besides direct patterning of 2D materials, BCP can also be used to create crested substrate to enhance the electron mobility of 2D TMD. The method is generally applicable to both p-type and n-type TMD materials, and compatible with traditional semiconductor manufacturing, could offer a significant boost for the wider application of the two-dimensional materials in semiconducting devices.


CHAPTER 7
Modeling and Optimization of Block Copolymer Self-assembly using Machine Learning

7.1 Introduction

As the current photolithography reached its resolution limit, block copolymer self-assembly has become one of the technologies that provides solutions for substitution [1–3]. Block copolymer (BCP), a polymer that has two or more different polymer blocks covalently bonded together, has the capability of generating a variety of ordered periodic structure at the scale of ~5 nm to 100 nm [4–7]. This large-area, low-cost fabrication method surpasses the electron-beam lithography in throughput and the conventional photolithography in resolution as well as cost. Although promising, the thermodynamically-driven self-assembling of BCP inherently possesses the problem of randomness which causes the presence of defects [8].

To address this issue, people has been using chemical or physical template to build the confinement that guides the BCP to form patterns with low defect density and long-range ordering [9–13]. Nevertheless, it has been shown the highly-
ordered pattern can be obtained intrinsically with proper process condition [7, 14], and thus the usage of templating could be reduced even removed. Several researches were focusing on tuning the process parameters to understand how the BCP morphology reacts to the variable of interest [15, 16]. In-situ experiments had also been carried out to reveal the morphology evolution during the self-assembly process [17]. However, the parameter space they experimented with were limited, and it is difficult to crack the interplay between different parameters. Simulation tools like SCFT have been great in providing guidance for finding the most stable morphology, but the scale of simulating system is relatively small and the parameters used are usually not directly transferable to the experiment [18].

On the other hand, machine learning and deep learning [19, 20], which have been massively used in building predictive model with historical data, are rapidly developed in the past decade and have achieved numerous successes in a variety of domain areas, such as image and speech recognition [21], system identification and control [22], quantum chemistry [23] and geoscience [24]. For example, convolutional neural network was reported to outperform experts in skin cancer and arrhythmia diagnoses [25, 26]. Several machine learning algorithms were widely incorporated into genetic and genomic research [27]. In materials science community, researchers have been using them in predicting material properties [28–30], searching potential rare-earth-free permanent magnets [31], and discovering new material compounds with desired property [32, 33]. Here we take the advantage of machine learning and deep learning as an alternative approach in modeling BCP self-assembly, and the optimal process parameters can be effectively found with the model.

In this work, we use the PS-b-PDMS diblock copolymer thin film as our model system to generate ordered nanostructure via solvent vapor annealing.
During each experiment, process parameters including the time-series data and the resulting morphology imaged by scanning electron microscopy (SEM) were collected. Machine learning and deep learning algorithms were employed to model the self-assembling process of the block copolymer, which took the process parameters as the inputs and the outputs predicted the resulting morphology and its quality metrics. Comparisons among different algorithms are provided and effects of different parameters have also been discussed.

7.2 Experimental

In the experiment, PS-b-PDMS with the molecular weight of 53 kg/mol ($\text{PS}_{37-\text{b-PDMS}}_{16}$) was firstly dissolved into cyclohexane (1 wt%) and then spin-coated onto silicon substrate with various film thicknesses ranging from 25 to 35 nm. The BCP thin films were subsequently solvent vapor annealed in a closed glass chamber with 5 cm in diameter and 4.5 cm in height, as shown in figure 7-1(a). The chamber contained a solvent reservoir of 4 cm$^3$ in volume which consists of either pure toluene or toluene/heptane with volumetric ratio of 4:1. The solvent vapor pressure was adjusted by a nitrogen flow through the chamber with the rate ranging from 0 – 20 sccm controlled by a mass flow controller. During the annealing, the BCP films would swelled into different thicknesses depending on the solvent vapor pressure. We have in-situ monitored the film thickness by spectral reflectometry (Filmetrics, F20-UV, 250–1500 nm) and recorded it in every 10 seconds. After annealing, the BCP films were reactive-ion etched by a 5s CF$_4$ plasma to remove the top PDMS surface layer and then a 22s O$_2$ plasma to remove PS as well as oxidized PDMS microdomains. At least 6 images were taken by SEM for each sample and ImageJ was used to characterize the quality metrics of the BCP morphology afterwards. In overall, 80 successful experiments were conducted.
with different process parameters. Figure 7-1(b)-(d) show the examples of BCP patterns we have obtained, including spheres, single layer cylinders and double layer cylinders (in which a second layer of lines sit in between two bottom layer cylinders). It is also common to see a mixture that two or three patterns coexist on a sample, as shown in figure 7-1(e).

![Figure 7-1](image_url)  
(a) The apparatus for solvent vapor annealing of BCP thin film. The swelling film thickness is in-situ monitored by spectral reflectometer. (b)-(e) Morphologies of (b) spheres, (c) single layer cylinders, (d) double layer cylinders and (e) a mixture of three patterns generated by PS$_{37}$-b-PDMS$_{16}$ under different solvent annealing condition.

To model the block copolymer self-assembly process with machine learning and deep learning algorithms, we break the problem down to three tasks. The first one is BCP pattern recognition, in which a classifier was built to distinguish the patterns we have obtained. And after slicing the original SEM image into grids, we could use the image classifier to identify the pattern in each grid and consequently acquire the overall areal proportion of each pattern. The second task is morphology prediction. We constructed a system that uses the provided process parameters to predict the areal proportion of each pattern in the resulting morphology. The last task is line pattern quality prediction, in which a model was built to predict the
resulting quality metrics of the line pattern by given process parameters and optionally the results from the second task. Only the line-forming samples were included in this task.

### 7.3 Block Copolymer Pattern Recognition

The goal here is to build a model that can recognize the BCP pattern in a SEM image. Nevertheless, instead of directly using the original SEM images, we cropped the images into small pieces (128 × 128 pixels) for the task. Figure 7-2(a) shows a few examples of images to be classified, where the spheres in the top row, the single layer cylinders in the second row, and the double layer cylinders in the bottom row. And we can see that images in the same category can still vary a lot in scale, orientation, and feature size. A total of 11640 images were collected, in which we randomly reserved 2400 for testing, 1200 for validation, and used the rest for training. Figure 7-2(b) shows the distribution of each pattern in each of the data set. Since we would not like to measure the model performance in bias to certain pattern, the amounts of each pattern were intentionally kept the same in the validation set and test set.

A convolutional neural network was employed to perform the image classification task. Figure 7-3 illustrates the high-level architecture of the network, which consists of three convolutional blocks and one fully-connected dense layer before output. For each convolutional layer, the filter size of 3 × 3 and the stride of 1 were used, and zero padding were added to the edge to maintain the image size. Rectified linear unit (ReLU) activation and batch normalization were applied after each convolutional layer. The number of filters for each convolutional block were 32, 64, and 128 respectively, starting from input to the output. At the end of each convolutional block, a maxpooling layer with the size of 2 × 2 and the stride
of 2 were used to reduce the image size to one fourth. A 64-unit dense layer were connected to the flattened output of the last convolutional block, followed by ReLU and batch normalization. Finally, the 3-unit dense layer and a softmax were used at last for the output.

Figure 7-2 (a) Example images of three BCP patterns in pattern recognition task. Top row: spheres. Second row: single layer cylinders. Third row: double layer cylinders. The images here are in different in scale, feature size and orientation as we want to mimic the practical situation and make the model more robust. (b) The data distributions of each pattern in the train, validation, and test data set.
Figure 7-3 Schematic of the architecture of convolutional neural network used for BCP pattern recognition.
The loss was calculated using categorical cross-entropy loss with a class weight which is inverse to the number of training samples in each class, and minimized by Adam optimizer (learning rate=0.001, the suggested values of beta_1 and beta_2 were used) during training. After training for 5-10 epochs, the model achieved 100% accuracy and a loss lower than $10^{-3}$ (figure 7-4) for the validation set. Further training could gradually lower the loss to the order of $10^{-4}$. The model with the lowest loss in the validation set was selected to be evaluated using test set, and again, 100% accuracy has been achieved. Even though the data set was relatively small, the model definitely demonstrated the capability in classifying the BCP pattern.

![Figure 7-4](image.png)  
Figure 7-4 The (a) categorical cross-entropy loss and (b) prediction accuracy of the train and validation data set in the training stage of CNN for BCP pattern recognition task. The accuracy has reached nearly 100% after training for 6 epochs.
7.4 Modeling of Self-assembly Process and Pattern Prediction

As the BCP morphology after annealing can be a mixture of two or three patterns, a model that uses process parameters and predicts the areal proportion of each pattern is of interest. In the experiment, we have varied the parameters including initial film thickness, anneal solvent ratio (the ratio between toluene and heptane), solvent vapor pressure (controlled by nitrogen flow rate) and time. The other parameters such as temperature, substrate surface energy were kept the same for simplicity. Among these parameters, solvent vapor pressure is a time-series parameter, which means it can be changed over time during the annealing process. Nevertheless, since the swelling film thickness is the actual key affecting the morphology and there is a delay from vapor pressure change to film thickness change, we have directly monitored the swelling film thickness during annealing and used it as our time-series parameter rather than solvent vapor pressure. Figure 4 shows the examples of different swelling film thickness versus time curves and the resulting proportions of each pattern. In general, there are a few points we would like to vary and understand the effects. The first one is whether to swell the film to a higher thickness (where order-disorder transition occurs) at beginning. Secondly, what is the swelling thickness to keep for the rest of annealing. And third point is how long we should wait for the annealing process. With these process parameters, we would like to predict the areal proportion of spheres, single layer cylinders, double layer cylinders and empty region. Note that the empty region, which means no pattern can be observed, was added because it might exist while dewetting happened.

A total of 80 valid samples was obtained in the experiment, in which 24 of them were reserved for testing. And because of the small data set, a seven-fold
cross-validation was employed for model parameter tuning. The model performance is measured by two metrics, the average of absolute proportion error and the self-defined accuracy, for which if the difference between actual label and prediction value is less than 10%, the prediction is considered to be accurate. Three different models including feedforward neural network, convolutional neural network and recurrent neural network were tried and compared, as detailed in the following paragraphs respectively.

The feedforward neural network (FNN) model was implemented with 2 hidden layers of 64 units in each layer and an output layer of 4 units. The exponential linear unit [34] was used as the activation function for the hidden layers to provide non-linearity and a softmax was applied to the output layer to get the bounded probability predictions that sum up to one. Since each dimension in the input vector is considered to be independent in FNN and a high dimensional input vector may make the network difficult to train given the limited samples, directly using the time-series swelling thickness curve in the inputs is not a great idea. Instead, we extracted some key features from the curve, such as the maximum swelling thickness and final swelling thickness. Combining the features from curve and the initial thickness, anneal solvent ratio and the timespan of keeping the same swelling thickness, we have derived 11 different features for inputting the FNN, as listed in table 1. For each feature, table 1 additionally shows the values of mean, standard deviation, minimum and maximum to give readers a glance of how the data was distributed in the training set. The distribution of the features in test set was generally the same as the training set (Table 2). Note that all the features were normalized by standard score before being fed into the model. While training, Kullback–Leibler (KL) divergence was used as the loss function and Adam optimizer was used to minimized the loss. The validation loss and absolute
proportion error have reached their minimum points after 20-50 epochs and start to increase afterwards (figure 7-5), indicating overfitting. Finally, the model with the lowest validation loss was evaluated with the test data, where the average proportion error of 6.9% and the prediction accuracy of 78.1% were achieved. The performance metrics on the other data set are also listed in table 3 as a reference.

Table 7-1 The process parameters used in training feedforward neural network for morphology prediction and the distribution statistics in the training set.

<table>
<thead>
<tr>
<th>Train</th>
<th>Init tks (nm)</th>
<th>Sol ratio</th>
<th>Time (min)</th>
<th>Max SR</th>
<th>Final Max tks SR</th>
<th>Final Max tks (nm)</th>
<th>1 / Max SR</th>
<th>Final tks *</th>
<th>Final tks * Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean</td>
<td>29.57</td>
<td>0.96</td>
<td>61.88</td>
<td>2.72</td>
<td>1.78</td>
<td>79.70</td>
<td>0.40</td>
<td>0.57</td>
<td>3222.11</td>
</tr>
<tr>
<td>std</td>
<td>2.63</td>
<td>0.08</td>
<td>36.03</td>
<td>0.77</td>
<td>0.24</td>
<td>20.49</td>
<td>8.16</td>
<td>0.11</td>
<td>1883.82</td>
</tr>
<tr>
<td>min</td>
<td>23.66</td>
<td>0.80</td>
<td>10.00</td>
<td>1.71</td>
<td>1.36</td>
<td>49.48</td>
<td>39.53</td>
<td>0.24</td>
<td>506.99</td>
</tr>
<tr>
<td>max</td>
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<td>1.00</td>
<td>160.00</td>
<td>4.15</td>
<td>2.67</td>
<td>124.15</td>
<td>82.01</td>
<td>0.59</td>
<td>8944.25</td>
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</tbody>
</table>

Table 7-2 The process parameters used in training feedforward neural network for morphology prediction and the distribution statistics in the test set.

<table>
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<tr>
<th>Test</th>
<th>Init tks (nm)</th>
<th>Sol ratio</th>
<th>Time (min)</th>
<th>Max SR</th>
<th>Final Max tks SR</th>
<th>Final Max tks (nm)</th>
<th>1 / Max SR</th>
<th>Final tks *</th>
<th>Final tks * Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean</td>
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<td>0.98</td>
<td>65.25</td>
<td>2.74</td>
<td>1.78</td>
<td>79.22</td>
<td>0.39</td>
<td>0.57</td>
<td>3373.05</td>
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<tr>
<td>std</td>
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<td>0.07</td>
<td>37.07</td>
<td>0.73</td>
<td>0.26</td>
<td>19.54</td>
<td>9.28</td>
<td>0.10</td>
<td>1997.38</td>
</tr>
<tr>
<td>min</td>
<td>23.66</td>
<td>0.80</td>
<td>10.00</td>
<td>1.71</td>
<td>1.36</td>
<td>50.43</td>
<td>37.15</td>
<td>0.25</td>
<td>478.83</td>
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<tr>
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<td>1.00</td>
<td>129.00</td>
<td>4.06</td>
<td>2.67</td>
<td>118.20</td>
<td>79.38</td>
<td>0.59</td>
<td>8367.99</td>
</tr>
</tbody>
</table>

Table 7-3 Summary of the performance metrics for each model in morphology prediction task.

<table>
<thead>
<tr>
<th>feedforward NN</th>
<th>Convolutional NN</th>
<th>Recurrent NN</th>
</tr>
</thead>
<tbody>
<tr>
<td>train</td>
<td>validation</td>
<td>test</td>
</tr>
<tr>
<td>avg. proportion error</td>
<td>3.28%</td>
<td>3.19%</td>
</tr>
<tr>
<td>accuracy</td>
<td>91.07%</td>
<td>92.50%</td>
</tr>
</tbody>
</table>
Figure 7-5 The (a) KL divergence loss, (b) average proportion error and (c) prediction accuracy of the train and validation data set in the training stage of FNN for morphology prediction task.

Convolutional neural network (CNN) had also been tried to perform the prediction task. In this model, the swelling thickness curve was directly used as the input, followed by four convolutional blocks, a dense layer of 128 units, and an output layer of 4 units with a softmax applied to it. Each convolutional block consists of two convolutional layers with kernel size 3, stride 1 and an average pooling layer of kernel size 2 and stride 2. The number of filters in each convolutional layer equals to $16 \times 2^n$, where $n$ is the $n^{th}$ convolutional block. As the same in FNN, the activation function of each layer was exponential linear unit, the loss was calculated by KL divergence and the whole network was updated using Adam optimizer. Since the swelling thickness curves are different in length (figure 7-6), zero values were padded in the front to unify the length to 968 pixels, which is the length of the longest curve in our data. After training around 100 epochs, the validation loss reached the minimum and started to rise up if the training continued (figure 7-7). The model with the lowest validation loss was tested and it exhibited an average proportion error of 8.5% and a prediction accuracy of 69.8%.
Figure 7-6 The swelling BCP film thickness monitored by spectral reflectometer during annealing. The number in parenthesis represents the areal percentage of each pattern.

Figure 7-7 The (a) KL divergence loss, (b) average proportion error and (c) prediction accuracy of the train and validation data set in the training stage of CNN for morphology prediction task.

Long-short term memory (LSTM) network, a type of RNN that gates both the inferences from the internal state and the input data, was utilized in the modeling. After input, three layers of 128-unit LSTM were stacked together, followed by a 128-unit dense layer and a 4-unit output layer. As the same as previous model, the exponential linear unit activation was applied to the dense
layer and a softmax was applied to the output to bound the probability prediction. It has been reported that the memory in a typical LSTM can only last tens of steps; as a result, reducing the 968 points of the swelling thickness curve is necessary. The curves were preprocessed by the rolling-window technique, where we included 24 points in each window and there was an overlap of 6 points between two neighboring windows. In each window, 9 statistical values based on the 24 points were calculated as the step input to the LSTM network. Eventually, a total of 53 steps were acquired after preprocessing. Figure 7-8 illustrates the sliding window method and the schematic structure of LSTM network. KL divergence and Adam optimizer were used again here for training, and after training for 50 epochs, the validation loss has reached its minimum (figure 7-9). The model with the lowest validation loss shows an average proportion error of 6.9% and a prediction accuracy of 78.1% on the test data.

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Figure 7-8 The schematic of the LSTM network (top part) used in morphology prediction task and the using of sliding window method (not to scale) to feed data into the network.
Figure 7-9 The (a) KL divergence loss, (b) average proportion error and (c) prediction accuracy of the train and validation data set in the training stage of LSTM network for morphology prediction task.

Table 3 lists all of the performance metrics of different models we have been using for the BCP morphology prediction task. Among the three models, the CNN exhibited a slightly worse performance, about 10% less in prediction accuracy and 1.5% more in average proportion error compared to the other two models. One possible reason is that the CNN takes pretty much the raw data as the input, which might be more difficult to learn compared with the preprocessed data that used by the other two models. In addition, CNN are known to be good at identifying features in curves and images, but it might be less sensitive to the value itself. On the other hand, the FNN and RNN model performed equally well in this task, showing similar results in both training and test data set. Although it is user’s freedom to choose a proper model, there are some comparison between these two models worth mentioning. The FNN is fast in training and prediction (~20s for 1000 steps of update), but the performance heavily depends on feature design and selection which requires a strong domain knowledge. It would be easy to miss some subtle features that is effective in prediction. In comparison with FNN, RNN is inherently suitable for temporal sequence data and has the freedom to learn to select the desired features of in the sequential data through training. Nevertheless,
it requires a longer training and prediction time (~120s for 1000 steps of update), which might be an issue in many application scenarios. In general, all the three models have exhibited the promising learning ability in the BCP self-assembly, and they could possibly be improved by having more data. However, as it is infeasible to image the entire sample area to get an accurate areal proportion of each pattern, and there exists the intrinsic variance in the annealing process, pursuing a model with extremely low prediction error is unrealistic.

To see the effect of each individual process parameter and answer the questions we proposed at beginning, dummy samples have been created to feed into model and see what would be the most likely results. The FNN model was used for simplicity. At each set of dummy samples, the variable of interest was varied, correlated variables were changed accordingly, and the independent variables were fixed. Figure 7-10 shows the predicted areal proportion of each pattern by varying different process parameters. In figure 7-10(a), it is clear to see that while the initial thickness of BCP film increases, the morphology would transit from single layer lines to double layer cylinders. And if the film is too thin, the empty region is likely to appear. In terms of the maximum swelling ratio (swelling thickness/initial thickness) during the annealing, the prediction shows it should be larger than 2 in order to get cylinders, otherwise sphere pattern is dominated, as shown in figure 7-10(b). Figure 7-10(c) shows the higher the final swelling ratio, the more chance one would get double layer cylinder pattern instead of single layer cylinder. At last, time is not sensitive in determining the areal proportion of the resulting morphology, as suggested by figure 7-10(d). In overall, this model not only made the predictions matched the empirical experience in the previous reports [16], but also fill the gap where experiments were not carried out. The optimal process
parameters for a desired BCP morphology can be easily obtained by grid search through the parameter space using the model.

Figure 7-10 The effects of (a) initial film thickness, (b) maximum swelling ratio, (c) final swelling ratio and (d) time on pattern areal proportion change predicted by feedforward NN.

7.5 Line Array Quality Prediction

As a low defect, high quality BCP pattern is the key to potential lithographic application, finding the optimal process parameters to obtain desirable morphology is essential. Ridge regression has been used in this task to correlate the pattern quality metrics of single layer cylinder and the process parameters as we listed in table 1. After training, predictions can be made with given process
parameters and the optimal condition can be found via grid searching the parameter space.

The same set of experiments as in the second task was used here; however, this time only the sample with areal proportion of single layer line larger than 50% was selected, resulting into 46 valid samples. Sixteen of them were reserved for testing. The quality metrics for each sample, including defect density, correlation length, line edge roughness, line width roughness, line width and periodicity, were characterized by its SEM images using ImageJ as well as the script provided by MurphysLab [35]. Figure 7-11 shows an example of the image analysis of the given single cylinder pattern and table 4, 5 summarizes the distribution of each quality metric over the train data and test data respectively. Process parameters were normalized prior fitting. For each pattern quality metric, different ridge regression models were fitted and the hyperparameter $\alpha$ of L2 penalty term was determined by cross-validation using leave-one-out method. The model performance was evaluated with $R^2$ score, which is defined as

$$R^2 = 1 - \frac{\sum (g_i - \bar{y}_i)^2}{\sum (y_i - \bar{y})^2},$$

where $g_i$ is the predicted value, $y_i$ is the true value and $\bar{y}$ is the mean of $y_i$. 

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Figure 7-11 Example of characterizing line pattern quality. (a) The original SEM image (b) Image with the defects marked (c) Orientation map (d) The fitting of correlation length, where the raw correlation data is shown in red and the smoothed data is blue.

Table 7-4 List of the distribution statistics of each pattern quality metric in the training data.

<table>
<thead>
<tr>
<th></th>
<th>Defect density ($\mu m^{-2}$)</th>
<th>Correlation length (nm)</th>
<th>Line edge roughness (nm)</th>
<th>Line width roughness (nm)</th>
<th>Line width (nm)</th>
<th>Periodicity (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean</td>
<td>64.20</td>
<td>715.35</td>
<td>1.55</td>
<td>2.44</td>
<td>18.41</td>
<td>40.39</td>
</tr>
<tr>
<td>std</td>
<td>74.33</td>
<td>647.46</td>
<td>0.21</td>
<td>0.41</td>
<td>3.84</td>
<td>1.03</td>
</tr>
<tr>
<td>min</td>
<td>6.96</td>
<td>56.18</td>
<td>1.19</td>
<td>1.71</td>
<td>9.21</td>
<td>38.21</td>
</tr>
<tr>
<td>max</td>
<td>380.57</td>
<td>2310.20</td>
<td>1.96</td>
<td>3.25</td>
<td>26.40</td>
<td>42.00</td>
</tr>
</tbody>
</table>

Table 7-5 List of the distribution statistics of each pattern quality metric in the test data.

<table>
<thead>
<tr>
<th></th>
<th>Defect density ($\mu m^{-2}$)</th>
<th>Correlation length (nm)</th>
<th>Line edge roughness (nm)</th>
<th>Line width roughness (nm)</th>
<th>Line width (nm)</th>
<th>Periodicity (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean</td>
<td>72.34</td>
<td>961.95</td>
<td>1.59</td>
<td>2.47</td>
<td>17.13</td>
<td>40.15</td>
</tr>
<tr>
<td>std</td>
<td>85.50</td>
<td>960.94</td>
<td>0.23</td>
<td>0.42</td>
<td>3.06</td>
<td>1.10</td>
</tr>
<tr>
<td>min</td>
<td>9.89</td>
<td>65.79</td>
<td>1.29</td>
<td>1.98</td>
<td>13.18</td>
<td>37.93</td>
</tr>
<tr>
<td>max</td>
<td>339.02</td>
<td>3170.51</td>
<td>1.95</td>
<td>3.23</td>
<td>23.88</td>
<td>41.93</td>
</tr>
</tbody>
</table>
Figure 7-12(a) shows the true and predicted values of defect density in each sample. The values in x-axis are meaningless but it was intentionally sorted by the true value of defect density for clarity. Although there were some discrepancies between the predicted value and the true value, the prediction generally followed the trend, even doing well with the sample of high defect density. The model has achieved the $R^2$ score of 0.678 on the test set, while the scores were 0.735 and 0.702 for the training set and the cross-validation respectively. From figure 7-12(b), we can see the inverse of maximum swelling ratio weighted the most among the parameters, which is reasonable since BCP can have more chance to attain lower energy state (fewer defects) if it has more space to move (higher swelling ratio). Nevertheless, the model also showed the maximum SR had a positive contribution to the defect density, which is in opposite to the previous point. We believe this contradiction is caused by the instability of the model and can be fixed by fitting with more data. Correlation length, the average distance over which orientational order is preserved that describes the degree of ordering in the film, is another important pattern quality metric we care about. As shown in figure 7-12(c), the model has performed quite well in predicting the correlation length, achieving the $R^2$ score of 0.849 on the training set, 0.722 on the cross-validation, and 0.826 on the test set. The model suggests the maximum film thickness and time are the two most important factors to the final result (figure 7-12(d)), which agrees well with our empirical experience. Moreover, the model also shows the final film thickness has significant contribution as well. This is understandable because the BCP would need space to move around during annealing, and if the swelled film is too thin, the BCP can only diffuse locally and not able to form long-range ordered pattern. The predictions for the other pattern quality metrics can be found in supporting
information, and table 6 summarizes the model performances on each quality metrics. In general, the model did not perform that well in the rest of quality metrics, and since we can neither intuitively see the relationship between the process parameters and the target quality metric, this result is imaginable.

Figure 7-12 (a)(c) The comparison of the true value and the model predicted value in defect density and correlation length respectively. (b)(d) The corresponding model coefficient in predicting (b) defect density and (d) correlation length.
Table 7-6 Summary of the $R^2$ score of predicting each pattern quality metric by ridge regression model.

<table>
<thead>
<tr>
<th></th>
<th>Defect density</th>
<th>Correlation length</th>
<th>Line edge roughness</th>
<th>Line width roughness</th>
<th>Line width</th>
<th>Periodicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>train</td>
<td>0.735</td>
<td>0.849</td>
<td>0.541</td>
<td>0.499</td>
<td>0.579</td>
<td>0.693</td>
</tr>
<tr>
<td>valid</td>
<td>0.702</td>
<td>0.722</td>
<td>0.075</td>
<td>0.294</td>
<td>0.353</td>
<td>0.539</td>
</tr>
<tr>
<td>test</td>
<td>0.678</td>
<td>0.826</td>
<td>0.526</td>
<td>0.344</td>
<td>0.297</td>
<td>0.569</td>
</tr>
</tbody>
</table>

7.6 Conclusion

To conclude, this work pioneered using machine learning and deep learning algorithms to model the BCP self-assembly process. Firstly, a convolutional neural network was built to recognize three different BCP patterns with 100% accuracy. And then, three different types of neural network were constructed to predict the areal proportion of each pattern in the resulting morphology using the process parameters during solvent vapor annealing. Over 75% accuracy and the average absolute proportion error under 7% were achieved. At last, the pattern quality of single layer lines was characterized with image analysis and ridge regression model was used to correlate the process parameters to each of the pattern quality metrics. The model showed good predicting capability in pattern defect density and correlation length, where the highest $R^2$ score over 0.8 was obtained. The machine learning and deep learning pipeline has demonstrated to be a great tool to capture the empirical experience and accurately predict the results. We believed it could be even more useful and reliable in the production line, where the large-scale data are collected. The potential physical relationship between the parameters and the results can also be inferred from the modeling.


[22] D. Zissis, E. K. Xidias & D. Lekkas, A Cloud Based Architecture Capable


doi:10.1038/npjcompumats.2016.28


[33] K. Fujimura, A. Seko, Y. Koyama, A. Kuwabara, I. Kishida, K. Shitara, C.


CHAPTER 8

Summary and Future Work

8.1 Summary

In this thesis, the nanolithography utilizing PS-b-PDMS diblock copolymer was discussed in a wide spectrum ranging from developing pattern transfer method, exploring the exotic size-dependent properties of materials after nanofabrication, and the unprecedented optimization technique to improve the BCP pattern quality. We started from demonstrating the universal pattern transfer methods for different application scenarios, including a Damascene process, a liftoff process and two ion-beam etching processes. The Damascene is suitable for patterning homogeneous film that could be deposited conformally, and the liftoff process allows the fabrication without etching the material, preventing the potential destruction. The ion-beam etching process is the most universal and may be applied in a variety of materials, especially beneficial for epitaxial films and multilayer stacks or materials that are hard to grow on a predefined mask. Structural analysis showed good fidelity during the ion-beam etching pattern transfer in terms of line width, LER, dot diameter and its standard deviation.

40 nm wide magnetic nanowires with in-plane and out-of-plane magnetic anisotropy were then fabricated using cylinder-forming PS-b-PDMS with ion-beam
etching process. In cobalt nanowire arrays, we have found although the DW interaction are dominated by the monopolar field, the dipolar field from the DW core still plays an important role in determining the magnitude and symmetry of the stray field near the wire. OOMMF simulation indicates DW interactions are sensitive to wire geometry and spacing. For DWs of the same sense in adjacent wires, the interaction behavior would largely depend on the competition between the monopole field and the dipole field. When the wires are thin and closely spaced, the dipolar field dominates and the DWs attract, but otherwise they repel. In [Co/Pd]15 and L10-FePt PMA nanowire arrays, the interaction causing by the stray fields from nearest neighbor wires is more essential. The stray field are predicted to drive domain wall motion producing antiparallel magnetization directions in adjacent nanowires. We have shown the Co/Pd nanowire has a highly correlated domain structure in which adjacent wires had antiparallel magnetization and domain wall locations were aligned, as a result of the magnetostatic interactions. In contrast, the L10-FePt nanowire only has a limited correlation between nearest neighbors, and this is believed to be the result of its ratio of stray field to coercivity is much lower compared to Co/Pd.

In addition to wires, CoFeB/MgO/CoFeB p-MTJ nanopillars with diameters of 64 nm and 25 nm were also. We have found magnetostatic interactions play an important role in coupling the hard and soft layers, especially for the smaller pillars. While the soft layer and hard layer in the 64 nm pillars reverse at different fields, the reversal of the two layers in the 25 nm pillars could not be distinguished. Moreover, the ion beam damage at the edges of the dots has attributed to the presence of a magnetically soft component of the pillars under hysteresis measurements.
We have also demonstrated the potential of incorporating of BCP lithography with 2D materials. Nanodots, nanorod and nanomesh features in monolayer MoS₂ are fabricated using BCP/PMMA as a removable mask. The photoluminescence measurement showed a decreased efficiency in nanodots compared to nanorods and nanomesh, which is attributed to the increasing in edge density. Also, the patterning process has resulted in a release of tensile strain that forms during the CVD growth and cooling process, confirmed by the peak shifting in Raman spectra. On the other hand, BCP lithography can be also used to create corrugated substrate surface. By make corrugations on SiO₂ dielectric surface, the electron mobility of MoS₂ has been enhanced by 5 times compared to the smooth SiO₂ substrates.

Lastly, the artificial neural network and ridge regression algorithm were used to model the BCP self-assembly process, allowing us to find the optimal processing parameters for the solvent vapor annealing. The model is able to obtain over 75% accuracy and under 7% of mean absolute error in predicting the areal proportion of each pattern in the resulting BCP morphology. Moreover, it also performed well in predicting the resulting cylinder pattern quality, achieving a $R^2$ score over 0.7 in predicting defect density and correlation length. We believe it is a great tool that is able to capture the empirical experience, and a key solution to industrial scale production using BCP lithography.

8.2 Future Work

a. Advanced BCP morphology and pattern transfer

Beyond thin film morphology, there are many more interesting 3-dimensional nanostructures that can potentially be acquired, either by BCP’s intrinsic bulk morphology or by creating a pre-constructed 3D surface for BCP to
form pattern on. For example, a spring-like structure has been obtained by assembling the BCP in confined space like tube. Nevertheless, due to the limited functionality of BCP, these structures are difficult to have practical application. It would be useful if these nanostructures can be converted into functional materials. Using similar idea as sequential infiltration synthesis [1, 2] may be an option but the problem of limited diffusion depth need to be solved. Another route such as designing functional polymer with self-assembly capability should also be considered.

b. Scaling effect of spin-orbit torque based switching

Spin-orbit torque (SOT) switching has become a popular research topic since it has great potential in high speed, energy economical spintronic device. Lots of demonstrations are on as grown thin films or on relatively large e-beam lithography patterned device. As the switching is accessed by domain wall motion, it would be important and interesting to see how does it respond to the devices with the size that are not large enough to have a domain wall, i.e. the size-dependent behavior. I would consider BCP as a great tool to fabricate the nanodevice, and thanks to the massive quantity fabrication, the measurement can be done in a more statistical manner.

c. Empirical modeling of block copolymer self-assembly

Although we have demonstrated the success in using machine learning and deep learning to model block copolymer self-assembly, the results are rather preliminary. Firstly, the model itself could be improved with more well-monitored experiment and more data. Also, in-situ characterization of BCP morphology could largely enhance the learning ability of the model. Most importantly, it can potentially be extended to a larger scope. For example, if we obtain a model
performed well in predicting PS-b-PDMS system, it is possibly to made a good model for PS-b-PMMA system out from PS-b-PDMS model, simply by providing the model a few examples showing the difference between these two system. It is because the two systems are sharing some common mechanisms in self-assembly. In this way, people will not need to do the whole experimental work again in order to find the optimal process condition. Simulation results from SCFT can also be learned by machine learning and deep learning, which would provide a better correlation between thermodynamic factors and the real parameters in experiment. Ultimately, a machine with a strong knowledge and experience in block copolymer lithography can be realized.