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Universal pattern transfer methods for metal nanostructures by block copolymer lithography

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Abstract

A universal block copolymer pattern transfer method was demonstrated to produce Co nanostructures consisting of arrays of lines or dots from a polystyrene-*block* -polydimethylsiloxane (PS-*b*-PDMS) diblock copolymer. Three processes were used: liftoff, a Damascene process, and ion beam etching using a hard mask of tungsten, including a sacrificial poly(methyl methacrylate) layer under the PS-*b*-PDMS for the etch and liftoff processes. The ion beam etch process produced the most uniform magnetic arrays. A structural and magnetic comparison in terms of uniformity, edge roughness and switching field distribution has been reported.

Introduction

Arrays of metal nanostructures with dimensions of a few nm and above, produced from thin films, are essential components of electronic[1], photonic[2], optoelectronic, and magnetic[3] 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[4], enabling applications in sensors[5], electronics[6–8], and superhydrophobic surfaces[9]. 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[2], or sequential infiltration synthesis to introduce metal selectively into one block, such as tungsten into poly(methyl methacrylate) (PMMA) blocks[10]. 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-*block*-polyferrocenyldimethylsilane (PS-*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[11]. Dot arrays were fabricated from CoCrPt films by using a PS-*b*-PMMA block copolymer pattern to make a spin-on-glass mask for ion beam etching[12,13]. Bit patterned media up to 1 Tdot/in² was made using a nanoimprint template, which had a lower density of features, to direct the self-assembly of PS-*b*-PMMA, and then transferring the pattern to CoCrPt nanodots by imprinting and etching. The density was extended to 3.2 Tdot/in² by substituting PS-*b*-PMMA with higher- χ polystyrene-*b*-polydimethylsiloxane (PS-*b*-PDMS) [14,15].

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-*b*-PDMS[16], and a similar process was used to make NiFe nanodots using polystyrene-b-polylactic acid (PS-*b*-PLA)[17]. 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[18,19]. Other additive process such as electrodeposition have also been reported[20–24].

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[11,25–36]. 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-*b*-PDMS block copolymer. Structural and magnetic comparisons of the cobalt nanostructures are reported in terms of uniformity, edge roughness and switching field distribution.

Experimental methods

A PS-*b*-PDMS diblock copolymer was selected for its high Flory-Huggins parameter[37] ($\chi_{PS-PDMS} = 0.14 - 0.27$ at room temperature[38,39]), 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[40–42]. 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[43–45]. The PS-*b*-PDMS used here (labeled as SD75) was synthesized and characterized as described in previous work[46]. The molecular weight was 75.5 kg mol⁻¹, the polydispersity index was 1.04, and the volume fraction of PDMS (f_{PDMS}) was 0.415. In bulk, this material forms a gyroid structure with domain spacing d₂₁₁ = 61 nm and unit cell parameter of 150 nm[45].

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 1a. 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 [44]. 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 [47]. 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 [45]. 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 CF_4 to remove the

PDMS surface layer (50 W, 15 mTorr, 10 sccm, in a Plasma-Therm 790) followed by 22 s of O_2 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 \pm 2 nm, row spacing 60 nm), in-plane cylinders (period 70 nm \pm 3 nm, row spacing 61 nm) and perforated lamellae (period 92 nm \pm 1 nm, row spacing 78 nm) shown in figure 1b, 1c, and 1d. 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[45].

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

	N ₂ flow rate	Solvent	Swelling	Annealing	Temp.	Period
	(sccm)	ratio	Ratio	time (hr)	(°C)	(nm)
		(T:H)	(SR)			
Spheres	2	10:1	2.3±0.1	2	25±1	69±2
Cylinders	5	5:1	1.5 ± 0.1	2	25±1	70±3
Perforated lamellae	2	3:1	2.2 ± 0.1	2	25±1	92±1





Figure 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.

Results and Discussion

A. 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[48]. The process demonstrated earlier[16] was adapted for the SD75 features, and is schematically shown in figure 2. A 110-120 nm thick cobalt film was conformally rf-sputtered on top of the oxidized-PDMS pattern (base pressure = 5×10^{-7} Torr, Ar flow rate = 20 sccm, Ar pressure = 2.2 mTorr, power = 200W, deposition rate = 0.13 nm/sec) and etched by a CF₄ reactive-ion etch (power = 450W, CF₄ 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 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 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 2. Schematic of Damascene-like pattern transfer process from BCP to metal nanostructures.



Figure 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 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.

B. 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 performated 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 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 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 $35^{\circ}\pm5^{\circ}$) 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





Figure 5. Schematic of liftoff pattern transfer process from a BCP mask using a sacrificial PMMA underlayer.



Figure 6. SEM images of cobalt nanodots and nanowires fabricated by lift-off process. The inset tilted views illustrate edge tapering.

C. Ion-beam Etch Process

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 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[49,50]. 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 $35^0\pm5^0$ taper angle, as shown in figure 8(b). An argon ion-beam was incident at a 55^0 angle to the rotating sample to gradually mill away the uncovered cobalt film (Ar pressure = 2×10^{-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 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 $25^0 \pm 3^0$ for cobalt dots and $40^0 \pm 5^0$ 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[51,52]. 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 7. Schematic of subtractive pattern transfer process from BCP self-assembled mask by ion-beam etch process



Figure 8. Plan 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.

D. Structural properties of Co arrays

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 = 6.7Å 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, LWR = $\sqrt{2}$ 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[53–64] 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.

E. Magnetic properties of Co arrays

The magnetic hysteresis loops of Co nanodots fabricated by the three different pattern transfer processes are compared in Figure 9, 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 2.71×10^{-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[31]. 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[31,65] 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[66]. 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 α 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 $\alpha = 0^{0}$, 30^{0} , 60^{0} and 90^{0} 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 ±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 10. 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. 10(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 elsewhere.

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

	DCD motherm	W hard mask	Co wires	Co wires	
Cynnders	BCP pattern	(liftoff)	(ion-beam etch)	(Damascene)	
Line width (nm)	36.8	33.4	49.7	42.05	
LWR (3o, nm)	5.6	7.3	7.4	13.06	
LER $(3\sigma, nm)$	8.5	5.7	6.1	10.22	
Doufounded lourslips	DCD nottom	W hard mask	Co dots	Co dots	
Perforated lamellae	BCP pattern	W hard mask (liftoff)	Co dots (ion-beam etch)	Co dots (Damascene)	
Perforated lamellae Diameter (nm)	BCP pattern 57.9	W hard mask (liftoff) 57.2	Co dots (ion-beam etch) 60.1	Co dots (Damascene) 55.8	
Perforated lamellae Diameter (nm) SD of diameter (nm)	BCP pattern 57.9 3.0	W hard mask (liftoff) 57.2 3.3	Co dots (ion-beam etch) 60.1 3.5	Co dots (Damascene) 55.8 4.2	



Figure 9. In plane hysteresis loops of cobalt nanodots patterned by three different processes compared to an unpatterned film.



Figure 10. 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).

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[67]. 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.

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