Thermal stability of $\text{L}_1^0$-$\text{FePt}$ nanodots patterned by self-assembled block copolymer lithography

To cite this article: Eduardo Fernandez et al 2018 Nanotechnology 29 465301

View the article online for updates and enhancements.
Thermal stability of L1₀-FePt nanodots patterned by self-assembled block copolymer lithography

Eduardo Fernandez¹,², Kun-Hua Tu¹, Pin Ho¹,³ and Caroline A Ross¹ ©

¹ Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Ave, Cambridge, MA 02139, United States of America
² BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain

E-mail: carross@mit.edu

Received 6 July 2018, revised 17 August 2018
Accepted for publication 31 August 2018
Published 21 September 2018

Abstract
Arrays of 14 nm thick L1₀-FePt nanodots with diameter of 27 nm and center-to-center spacing of 39 nm were produced by block copolymer patterning of an FePt film and their magnetic reversal and thermal stability were characterized. A self-assembled polystyrene-b-polydimethylsiloxane diblock copolymer film was used as a lithographic mask and a pattern transfer process based on ion beam etching and rapid thermal annealing of the sputtered FePt film was developed. The dot arrays exhibited perpendicular magnetic anisotropy with \( K = 4.8 \times 10^7 \) erg cm\(^{-3}\) and a saturation magnetization of 960 emu cm\(^{-3}\). First order reversal curves indicate a softer magnetic component attributed to the ion-milled material at the edges of the dots. The switching volume and the thermal stability were obtained from relaxation measurements and DC demagnetization curves. Micromagnetic simulations reproduce the magnetic domain structure obtained for the continuous and patterned FePt thin film.

Keywords: magnetic switching volume, L1₀ structure, block copolymer lithography, PS-b-PDMS, pattern transfer

(Some figures may appear in colour only in the online journal)

1. Introduction

The thermal stability of magnetic nanostructures is an essential characteristic of magnetic memory, biological labeling, hyperthermia treatments and other applications [1–4]. Thermal stability is related to the probability that thermal fluctuations can induce spontaneous reversal of the magnetization, which occurs when the thermal energy \( kBT \) is a large enough fraction of the energy barrier for reversal [5]. Raising the temperature facilitates reversal, both by increasing thermal energy and by reducing the energy barrier. For example in heat assisted magnetic recording [6, 7], local heating of a region of a high anisotropy magnetic recording medium lowers the energy barrier to the point that the field of the write head is capable of writing data on the medium. This enables the use of hard magnetic materials such as CoCrPt, FePt, CoPt, or FePd [5–11] for recording media which can have coercive fields over \( \mu_0H_c = 3 \) T after patterning, above the maximum field of ~2.4 T that a write head can apply.

Thermal stability may be expressed by a factor \( \Delta = KV^* / kT \), where \( K \) is the magnetic anisotropy, \( V^* \) is the switching volume [5, 12], and \( kT \) is thermal energy. \( V^* \) represents the volume of magnetic material involved in the reversal process. For a uniaxial particle undergoing coherent rotation, \( V^* = V \), where \( V \) is the physical volume of the particle, but incoherent reversal leads to \( V^* < V \). In systems where particles are magnetically coupled, \( V^* \) may exceed \( V \) as multiple particles switch together. A criterion for stability is
Δ > 40, ensuring that the magnetic nanostructure will maintain its magnetization direction for ~10 years. There have been numerous reports on the thermal stability of nanoparticle systems [13], but lithographically patterned 2D arrays of thin film magnetic nanostructures provide a particularly well controlled model system to examine switching mechanism and thermal stability. 2D arrays are also of interest for bit patterned media, where the magnetization direction of each particle represents one bit of data [14, 15]. This article examines the thermal stability and magnetic reversal of 2D arrays of high anisotropy L10 structure FePt thin film dots.

In order to pattern 2D arrays of magnetic nanostructures, several methods have been used including embedded mask patterning, electron beam lithography, nanoimprint lithography, and block copolymer (BCP) self-assembly [16–18]. The latter process, which relies on the microphase separation of a BCP thin film, is a promising strategy for cost-effective fabrication of nanoscale structures with periodicities below 100 nm. The BCP consists of two covalently bonded but immiscible blocks, and annealing leads to the formation of e.g. spheres, cylinders or lamellae of one block within the second block, driven by the segregation strength, χN, where χ represents the segment–segment Flory–Huggins interaction parameter and N represents the degree of polymerization [19]. To control the long-range order and orientation of the self-assembled nanostructures in BCP thin films several annealing and ordering techniques have been applied including thermal annealing [20, 21], electric fields [22], the use of chemical and topographical substrate patterns [23–26], shear alignment [27] and solvent vapor annealing [28, 29]. The microphase-separated structure can be used for additive or subtractive lithography processes by typically removing one block and using the remaining structure as a mask.

Prior work has demonstrated the use of BCP lithography to pattern arrays of magnetic materials including NiFe, CoCrPt or Co/Pd [30–33], but there has been little work on patterned arrays of L10 materials. FePt L10 dots were made previously using BCP lithography [34] but the structural and magnetic characteristics were not explored in detail. We recently described patterned line arrays of FePt made using BCP lithography [35], but the process was limited by the roughness of the FePt after annealing. Here we use BCP lithography to make arrays of L10 FePt dots and measure the thermal stability from the time-dependent coercivity and the interparticle interactions via the first order reversal curve (FORC) method. Application of BCP patterning technology to high anisotropy thin film materials such as FePt will facilitate the development of high density recording media as well as an improved understanding of the thermal stability of hard magnetic nanostructures.

2. Fabrication and characterization methods

The dot arrays are prepared from L10 FePt films in a process shown schematically in figure 1. The 14 nm thick FePt films were deposited on MgO (100) substrates using ion beam sputtering with a base pressure of 5 × 10⁻⁸ Torr. The samples were grown at room temperature leading to a chemically disordered face centered cubic (fcc) A1 phase. In order to produce the ordered face centered tetragonal (fct) L10 phase with alternating Fe and Pt atomic planes along the [001] c-axis, the samples were subjected to a rapid thermal anneal (RTA) at 700 °C for 300 s in N2 ambient at different stages of the fabrication process. The transformation from the A1 to L10 structure was characterized by x-ray ω-2θ diffraction measurements (PANalytical X’Pert PRO x-ray diffractometer with Cu Kα radiation).

16 nm of carbon was deposited by electron beam evaporation on the FePt films. This carbon layer is used as a mask for the subsequent patterning process via ion beam etching. A 30 nm thick film of polystyrene-block-polydimethylsiloxane (PS-b-PDMS, purchased from Polymer Source) was spin coated on top of the carbon layer. The BCP had a molecular weight of 56.1 kg mol⁻¹ with a polydispersity of 1.1, and a PDMS volume fraction (fPDMS) of 0.161. The BCP wets the carbon, and there was no need to coat a brush layer of hydroxyl-terminated PS or PDMS to avoid dewetting as has been performed in previous work [36–38]. The BCP film was annealed at room temperature in a vapor of pure toluene for 10 min in a closed glass chamber with a volume of 88 cm³ containing 3 cm³ of liquid toluene. Based on in situ spectral reflectometry measurements (Filmetrics, Inc. F20-UV 250–1500 nm), the BCP swelled from 30 to 52 nm thickness on exposure to the vapor, giving a swelling ratio of 1.7 (figure 2(a)). After the vapor annealing the sample was heated for 2 min at 60 °C to remove the solvent. The BCP films were then reactive-ion etched for 5 s in CF4 to remove the PDMS layer at the air interface, followed by 80 s of O2 plasma to remove the PS block leaving an array of oxidized PDMS close packed spherical microdomains. The O2 plasma process also etches the carbon layer beneath the PS creating the hard mask, consisting of bilayer dots of oxidized PDMS/carbon on top of the magnetic film [39].

The samples were imaged using a Zeiss Merlin high-resolution scanning electron microscope (SEM) at 2 kV, and ImageJ software [40] was used to obtain the size and distribution of the dots. The oxidized PDMS/carbon dots had a diameter of 27 nm and center-to-center distance of 39 nm (figure 2(b)). The dots had a narrow distribution of diameters with a standard deviation of 1.4 nm, shown in the inset of figure 2(b). The dots occupy 56.5% of the total surface and have a density of 0.63 Tdot in⁻².

The sample was then etched using an Ar⁺ ion beam in increments of 30 s. Since the MgO is non-conductive, measurements of the electrical resistance after each ion beam etching step indicated the completion of the etching process. An etching time of 2 min led to a resistance increase from 0.3 kΩ to 0.8 MΩ. The resulting metal dot array is shown in figure 2(c). Magnetic measurements were made using a vibrating sample magnetometer (VSM, ADE model 1660), a SQUID magnetometer (MPMS3-Quantum Design) and a torque magnetometer (ADE model 1660), and surface topography was measured using a Nanoscope IV atomic force microscope (AFM).
3. Results and discussion

3.1. Structure and magnetic hysteresis of L1₀ FePt continuous thin film

The cubic MgO has a lattice parameter of 4.212 Å (figure 3, red line). The as-deposited FePt showed no film peaks in the diffraction scans. However, diffraction peaks from the annealed FePt yielded an out-of-plane (OP) lattice parameter of 3.70 Å (figure 3, black line). This lattice parameter is close to the bulk lattice parameter \( c \) for L1₀ FePt, which is a P4/mmm fct structure with \( c = 3.713 \) Å and \( a = b = 3.853 \) Å. There are no \((h00)\) peaks in the thin film scan corresponding to the \( c \) spacing, which is consistent with the film having a \( c \)-axis out of plane texture. The high perpendicular magnetic anisotropy, discussed below, supports the interpretation of the annealed structure as textured fct rather than a cubic disordered phase.

VSM measurements show that for the unannealed A1 phase sample the magnetization is mainly in plane due to shape anisotropy (figure 4(a), red line). The small hysteresis in the hard-axis OP loop may indicate that a fraction of the L1₀ phase has crystallized. After annealing, the sample shows a sheared OP hysteresis loop (figure 4(b), black line) with coercivity 2 kOe. The saturation magnetization (\( M_s \)) for the annealed film was 960 emu cm\(^{-3}\), compared to the \( M_s \) value of 1150 emu cm\(^{-3}\) reported for epitaxial L1₀ FePt films [41]. The in-plane (IP) loop also shows hysteresis with a coercive...
A key issue in patterning the FePt film arises from the film roughening during the RTA required to form the ordered phase. As shown in the insets of figure 3, an unpatterned film before RTA has a smooth surface with a root mean square roughness of 0.2 nm (figure 4(a)), but the roughness increased to 3 nm after it was annealed (figure 4(b)). The surface roughness interferes with the self-assembly of the BCP, leading to poorly ordered dot arrays. To attempt to limit roughening, a thin Ta layer was deposited on top of the FePt prior to annealing, but this diffused during RTA and lowered $M_s$ of the FePt significantly.

The strategy adopted was therefore to form the BCP pattern consisting of carbon/oxidized PDMS dots on the FePt film prior to annealing. In our first attempt the RTA was performed between etching the BCP and the ion beam etching (i.e. RTA between steps 5 and 6 of figure 1), but the resulting dot arrays did not exhibit a high perpendicular magnetization. Both the IP and OP hysteresis loops exhibit high coercivity but the magnetization reached only about 400 emu cm$^{-3}$, which is lower than expected from the areal coverage of the dots. The low saturation magnetization is attributed to incomplete saturation of the sample at the maximum field used in the VSM measurement, i.e. the loops represent minor loops. To obtain dots with a higher PMA, the process was modified by performing the RTA after ion beam etching (i.e. RTA after step 6). The optimum process is therefore: FePt deposition, carbon deposition, BCP deposition and annealing, reactive ion etching of BCP and carbon, ion beam etching of FePt to form the dot array then RTA to crystallize FePt. The magnetic results from this improved process are described in the next subsection.

3.3. Magnetic hysteresis of $L_{10}$ FePt patterned film

SQUID magnetometry measurements are shown in figure 5 for a dot array sample made by ion beam etching followed by RTA. The measurements were made on a 5 mm diameter section cut from the central area of the original 10 mm square sample. Based on the dimensions of the dots (diameter of 27 nm and center to center distance of 39 nm), the OP curve (figure 5, black line) indicates $M_s = 930$ emu cm$^{-3}$, similar to that of the annealed continuous thin film and consistent with formation of the $L_{10}$ phase. The OP loop exhibits a high remanence and a coercivity of 14.8 kOe, in comparison with 2 kOe for the continuous thin film (figure 4(b), black line). The larger coercivity of the patterned sample compared with the unpatterned film originates from a different reversal process for the dots (e.g. single domain behavior in the dots versus domain wall propagation in the unpatterned film), or a higher anisotropy in the $L_{10}$ phase arising from the lower in plane stress of the dots during the annealing process. The IP loop (figure 5, red line) was not saturated even at 80 kOe.

Figure 4. Magnetic hysteresis loops of an unpatterned sample of FePt/MgO for an in-plane field (red line) and an out-of-plane field (black line). Left: before rapid thermal annealing, and right: after rapid thermal annealing. The insets show the corresponding AFM images.

Figure 5. Magnetic hysteresis loops of FePt dots annealed after ion beam etching for an in plane field (red line) and an out of plane field (black line).
There is a low field step in both OP and IP loops whose origin may be one of the following: regions where patterning was incomplete and the film coercivity is lower; a region with reduced anisotropy at the edges of the dots where the chemical ordering was degraded; or incomplete conversion of grains of the A1 phase to the L10 phase. (A similar step was observed for the sample that was annealed before ion beam etching.) FORC measurements were used to help distinguish between these possibilities. The FORC plots are constructed from analysis of the ascending branches of the hysteresis loops and are plotted in terms of the coercivity $H_{c1}$ and bias field $H_b$. (or interaction) field $H_b$, of the population of hysteron that constitute the hysteresis loops.

The FORC measurement of the annealed unpatterned film (figure 6(a)) exhibited only one peak, and together with the x-ray data, argues against the presence of substantial amounts of the A1 phase after annealing. The FORC of the patterned sample (figures 6(b) and (c)) exhibits two contributions, the softer one with $H_{c1}$ around 5 kOe, and the harder one with $H_{c1}$ around 20 kOe. The dominant feature in the FORC is a narrow ridge along the $H_{c1}$ axis with zero bias $H_b$. This pattern is characteristic of an ensemble of non-interacting single domain particles [44–46]. The lower intensity peak at 5 kOe shows a non-zero $H_b$ indicating a magnetic interaction with the high coercivity material. This suggests it does not originate from regions of incomplete patterning, which would only interact with the dots via weak dipolar interactions, but instead it is attributed to a low anisotropy region at the boundaries of the dots, which forms as a result of Ar ion damage and implantation [47]. The softer material at the boundary is expected to be exchange-coupled to the harder material at the center of the dot, leading to the bias field. In this model, only 1.5 nm thickness of low anisotropy material at the dot edges would be needed to account for the height of the low field step in the hysteresis loops. Preparing dots of different sizes would enable this hypothesis to be validated, since the fraction of low-anisotropy surface material is lower for larger dots.

3.4. Magnetic switching volume of L1$_0$ FePt patterned film

Assuming coherent reversal of the dots with anisotropy $K = 4.8 \times 10^7$ erg cm$^{-3}$, the thermal stability of $\Delta = KV/\kappa T$ may be estimated as $\sim 9000$, assuming $V$ equals the physical volume $V$ of the dots for a coherent reversal process ($V = 8.0 \times 10^{-15}$ cm$^3$ from the diameter of 27 nm and thickness of 14 nm). However, incoherent reversal as well as the presence of material with lower anisotropy at the edges of the dots will reduce the thermal stability. To obtain a measurement of the switching volume, time-dependent measurements of the magnetization were carried out. Magnetization relaxation due to irreversible jumps of single domain macrospins is assumed to follow an Arrhenius-type relaxation. The magnetization decreases logarithmically with time as $M(t) = M(0) - \Delta \ln(t/\tau_0) \propto t^{-2}$, with the slope defined as the magnetic viscosity, $S$. $S$ depends on the distribution of the activation energies of the macrospins under a given external magnetic field. In addition, the application of a reverse field (oriented opposite to the local magnetic moment) induces reversals whose number depends on the field itself and also on the distribution of activation energies.

By recording the remanent magnetization as a function of reverse fields of increasing amplitude (the demagnetization curve (DCD) figure 7(b), green line), the number of irreversible jumps per unit field (the irreversible susceptibility $\chi_{DCD}$) can be obtained. This parameter contains an explicit dependence on $V$, which can be extracted from the ratio $\chi_{DCD}/S$, where the values of $\chi_{DCD}$ and $S$ correspond to the reversal field for which both quantities are maximum [48, 49]. To measure DCD as well as viscosity, the sample is driven to positive saturation prior to the application of a reverse magnetic field. In the inset of figure 7(a) we show the magnetic viscosity and on figure 7(a) blue line the irreversible susceptibility at room temperature, both having

![Figure 6](image-url)
maximum values at 20 kOe and as a function of the reverse field.

We obtained a switching volume of $3.7 \times 10^{-25}$ m$^3$ (the volume of a cube with a 7 nm edge) and a thermal stability $\Delta = 428$. For a data retention time of about 10 years, $\Delta = 40$ [50] is required, which would correspond to a (3.7 nm)$^3$ cube, assuming the same anisotropy and neglecting low-anisotropy material at the edges. BCP lithography could be extended to making arrays with period below 10 nm [51] which would be close to the limit of thermally stable FePt dots presented in this work.

3.5. Micromagnetic simulations

Micromagnetic simulations of the domain structure and stray field of the FePt film and dots were carried out. The micromagnetic simulations were performed using the finite difference OOMMF code [52]. The film plane (the xy plane) was modeled using 2D periodic boundaries with a box size of $1 \mu m \times 1 \mu m \times 30$ nm, consisting of 10 repeats of the xy plane, to avoid effects from the edges of the film. The mesh used had a lateral cell size of 2.5 nm and cell thickness of 2 nm. The model used values of $M_S = 960$ emu cm$^{-3}$ and $K = 4.9 \times 10^7$ erg cm$^{-3}$ based on our experimental measurements, an exchange stiffness of $A = 1 \times 10^{-5}$ erg cm$^{-1}$ [53], and a damping parameter of 0.1. The FePt layer was modeled as a set of grains, each with 20 nm diameter (area of 400 nm$^2$), and each of which had a common anisotropy axis with a random misalignment of 5° with respect to the OP direction. The FePt was 14 nm thick, and the model included 16 nm of non-magnetic material above the film in which the stray field was calculated.

Figure 8(a) shows the OOMMF simulation of the stray field 16 nm above the surface of the film after initially
randomizing the directions of the magnetic moments in the cells then allowing the model to relax. This may be compared with figure 8(b) which shows an experimental magnetic force microscope image of an unpatterned annealed film sample after ac-demagnetization, taken by a Quadrexed D3100 Nanoscope IV AFM with a low moment CoCr magnetic probe at a working distance of 10 nm and a scanning area of 1 μm². The experimental ac-demagnetization was carried out in an OP field of up to ±14 kOe with the field decreasing in 10 Oe steps. Both the experiment and simulation show a labyrinth pattern of domains with widths on the order of 50 nm. Figure 8(c) shows the domain wall structure, in which about 90% of walls are 180° Bloch domain walls with width of ~5 nm, which is characteristic of samples with high perpendicular anisotropy. Figure 8(c) also shows a section through a small bubble domain in which part of the wall has Néel character. We also simulated a full hysteresis loop including the virgin curve calculated from (b); (d) dot magnetization along the z direction at the point in the hysteresis loop indicated in (c). Blue dots have reversed; red have not.

Figure 9. (a) SEM image of FePt dots, (b) and bitmap image used for the OOMMF simulation that assigns a different 5° misorientation of the easy axis of each dot with respect to the out-of-plane direction. The easy axis directions are shown in different colors as depicted in the inset: the black dots have an OP easy axis and the colored dots have easy axes tilted 5° along x (blue), y (green), −x (yellow) or −y (red). (c) Modeled hysteresis loop including the virgin curve calculated from (b); (d) dot magnetization along the z direction at the point in the hysteresis loop indicated in (c). Blue dots have reversed; red have not. The FePt dots were modeled using the same parameters for K, Ms, exchange and damping as the unpatterned film, but taking a 1 μm × 1 μm SEM image of the dot array (figure 9(a)) as a mask to define the FePt dots in the model. Each dot had a 5° deviation of its anisotropy axis assigned randomly along an IP direction. The different directions are shown in color in figure 9(b). A hysteresis loop was obtained for an out of plane field of up to 120 kOe, figure 9(c). This yielded a switching field of 60 kOe which is four times larger than the measured value of 14.8 kOe. The high value found for the model may be a result of not including the low anisotropy material at the edges of the dots, but the cell size in OOMMF was too large to allow the thin layer at the edges to be included. On cycling through the hysteresis loop, most dots switched at approximately the same field but there was a step in the loop representing a state in which a few of the dots were stabilized in the unreversed state. This configuration is shown in figure 9(d) where the reversed dots are blue and unreversed dots are red. The model suggests that a coherent
reversal process occurs, and domain walls were not present within the dots during reversal.

4. Conclusions

The magnetic behavior of 14 nm thick L10 FePt films and dot arrays was investigated. Annealing the as-grown FePt film produced the ordered fct L10 phase. Close packed dot arrays were made using BCP lithography with a carbon hard mask. In the optimum BCP lithography process, the RTA was carried out after the FePt had been patterned by ion beam etching, producing 27 nm diameter dots with perpendicular magnetic anisotropy. Hysteresis measurements and FORC plots indicate a soft magnetic phase in the dots which was attributed to a poorly-ordered region at the edges of the dots. An analysis of the switching volume gave a thermal stability of $KV/KT = 428$ at room temperature. This suggests that patterned L10 FePt dots could be scaled to few-nm dimensions and still retain sufficient thermal stability for a 10 years data retention time.

Acknowledgments

The authors gratefully acknowledge the support of C-SPIN, a STARnet Center of the Semiconductor Research Corporation sponsored by DARPA and MARCO. EF acknowledges the Agency of Science, Technology and Research Basque Government Fellowship grant and PH acknowledges sponsored by DARPA and MARCO. EF acknowledges the STARnet Center of the Semiconductor Research Corporation.

ORCID iDs

Caroline A Ross https://orcid.org/0000-0003-2262-1249

References

[6] Challener W A et al 2009 Heat-assisted magnetic recording by a near-field transducer with efficient optical energy transfer Nat. Photon. 3 220–4
[13] Chen M and Nikles D E 2002 Synthesis, self-assembly, and magnetic properties of Fe$_x$Co$_{1-x}$Pt$_{200-x-y}$, nanoparticles Nano Lett. 2 211–4
[17] Seung H K et al 2007 Direct nanoimprinting of metal nanoparticles for nanoscale electronics fabrication Nano Lett. 7 1869–77
[31] Hellwig O et al 2010 Bit patterned media based on block copolymer directed assembly with narrow magnetic switching field distribution Appl. Phys. Lett. 96 052511
[37] Park C, Yoon J and Thomas E L 2003 Enabling nanotechnology with self-assembled block copolymer patterns Polymer 44 6725–60
[40] Abramoff M D, Magalhaes P J and Ram S J 2004 Image processing with ImageJ Biophotonics Int. 11 36–42
[43] Barmak K 2005 On the relationship of magnetocrystalline anisotropy and stoichiometry in epitaxial L10 CoPt (001) and FePt (001) thin films J. Appl. Phys. 98 033904