High-Density Periodically Ordered Magnetic Cobalt Ferrite Nanodot Arrays by Template-Assisted Pulsed Laser Deposition

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A novel nanopatterning method using pulsed laser deposition through an ultrathin anodic aluminium oxide (AAO) membrane mask is proposed to synthesize well-ordered nanodot arrays of magnetic CoFe_2O_4 that feature a wide range of applications like sensors, drug delivery, and data storage. This technique allows the adjustment of the array dimension from ~35 to ~300 nm in diameter and ~65 to ~500 nm in inter-dot distance. The dot density can be as high as 0.21 Terabit in.\(^2\). The microstructure of the nanodots is characterized by SEM, TEM, and XRD and their magnetic properties are confirmed by well-defined magnetic force microscopy contrasts and by hysteresis loops recorded by a superconducting quantum interference device. Moreover, the high stability of the AAO mask enables the epitaxial growth of nanodots at a temperature as high as 550 °C. The epitaxial dots demonstrate unique complex magnetic domains such as bubble and stripe domains, which are switchable by external magnetic fields. This patterning method creates opportunities for studying novel physics in oxide nanomagnets and may find applications in spintronic devices.

1. Introduction

The hard ferrite spinel CoFe_2O_4 (CFO) has been intensively investigated for its large magnetocrystalline anisotropy and magnetostriction, chemical stability, and unique nonlinear spin-wave properties, as well as for its application potentials in spintronic devices, for example, magnetic sensors or memories.\(^[1-4]\) It has also been considered as a main component for multiferroic multilayers and composites.\(^[5]\) Nanometer-size CFO structures have also been one of the most frequently chosen systems for studying nanomagnetism. They show high potential for some important applications, ranging from data storage, sensors, and drug delivery to bimolecular tagging, imaging, sensing, and separations.\(^[6-10]\) Up until now, a large variety of nanostructures like monodisperse particles,\(^[^7,11]\) wires,\(^[^12]\) curved bowls,\(^[^13]\) and hollow spheres\(^[^14]\) have been fabricated, and they demonstrate several unique structure–property relationships.\(^[^15-18]\) All these state-of-the-art investigations are paving the way from basic research to industry applications.

For spintronic devices, a fundamentally essential step is to fabricate ordered arrays of nanomagnets on appropriate substrates, as required by the emerging information technologies such as ultrahigh density storage devices, sensors, magnetic random access memory devices, and logic devices.\(^[^19,20]\) Although an increased interest exists in metal-based patterned magnets driven by modern lithography techniques in recent years, there are still only a few reports on patterned oxide magnets, probably due to their refractory and chemical inertness and the lack of a suitable fabrication process for high-density and large-area nanodot arrays.

In this work, a combined top-down and bottom-up patterning technique involving pulsed laser deposition (PLD) and ultrathin nanoporous anodic aluminum oxide (AAO) membranes as stencil masks was employed to fabricate large-area nanosized CFO dot arrays. The AAO-based method is a unique approach for the direct growth of nanostructures at relatively high temperatures (up to \(550 °C\)), enabling a high degree of control of the crystalline quality.\(^[^21,22]\) The lift-off process can be solvent-free, thus avoiding cross-contamination during nanopatterning. We successfully fabricated well-ordered CFO arrays with diameters of nanodots ranging from 35 to 300 nm and an area density near 0.21 Terabit in.\(^2\). Moreover, we have been able to achieve epitaxial nanodot structures by carefully adjusting the deposition parameters.

2. Results and Discussion

2.1. Microstructures of CFO Nanodot Arrays

The nanodot array is fabricated based on PLD through an ultrathin AAO template mask, as schematically illustrated in the flow chart of Figure 1a. A conducting layer of SrRuO_3 (SRO) was deposited,
then the AAO mask was transferred, followed by depositions of CFO using PLD. Finally the mask was removed and the ordered nanodot array was obtained. A representative atomic force microscopy (AFM) image of the resulting sample nanodot array is also shown in Figure 1b, which exhibits a well-ordered hexagonal arrangement of nanodots with an average diameter of ~50 nm and an interdot distance of ~104 nm.

Figure 2 shows scanning electron microscopy (SEM) images of nanodot arrays in different states of preparation, beginning with a SrTiO3 (STO)/SRO substrate covered with an AAO mask. Figure 2a shows the CFO mask before deposition, which includes periodically ordered circularly shaped holes. Throughout this work we used self-organized AAO. Perfectly ordered AAO membranes and long-range ordered nanodot arrays could also be fabricated by imprint and other methods.[21,23,24] The CFO was then deposited on the above substrates at a temperature of 450 °C and a vacuum of about 10−5 mbar to ensure that the CFO material properly reaches ambient pressure, making the fabrication of high-quality epitaxial CFO was then deposited on the above substrates at a temperature of 450 °C and a vacuum of about 10−5 mbar to ensure that the CFO material properly reaches ambient pressure, making the fabrication of high-quality epitaxial

The magnetic properties of the nanodot array were characterized macroscopically by superconducting quantum interference device (SQUID) measurements and locally by magnetic force microscopy (MFM). Figure 5 shows both AFM topography and MFM images of nanodot arrays with diameters ranging from 35 to 300 nm and inter-dot distances from 60 to 500 nm were achieved. The dot height can be varied in the range from a few up to a hundred nanometers by carefully controlling the deposition rate and duration. If we consider a single dot as one functional unit for potential devices (e.g., data storage), the memory density can reach as high as near 0.2 Terabits in.2 based on the calculation for a hexagonal array with an inter-dot distance of 60 nm.[21]
mentioning that in-plane magnetization may also exist in the dots and contribute to the MFM contrast, but its interaction with the tip would be much weaker compared to the out-of-plane component. The observed dark–bright contrasts in MFM images are most likely from an out-of-plane component of magnetization at remanent state, which is switchable by a perpendicular magnetic field.

Figure 6 shows magnetic loops taken by SQUID along both in- and out-of-plane directions from a dot array with a dot diameter of 50 nm, an interdot distance of 104 nm, and a height of 40 nm. In both directions, relatively slim loops can be observed, indicating that the dots are soft magnets in nature. The out-of-plane loop shows a smaller remanent magnetization than that of the in-plane loop, implying a slightly in-plane easy axis. From the inserted enlarged loops, the in-plane coercive field can be determined as around ~170 Oe, which is much smaller than that of an epitaxial CFO film on a SRO/STO substrate (~3,000 Oe). \[26\] In epitaxial CFO films, the large coercivity can be ascribed to magnetostrictive, magnetocrystalline, and shape anisotropies, among which the magnetostrictive anisotropy from clamping strain is the dominating factor. \[3,26\] In our CFO islands, the magnetostrictive anisotropy can be greatly reduced by fast relaxation of the strain from the island edges, while the shape anisotropy and crystalline anisotropy can be released by forming noncontinuous islands and polycrystallites, respectively. Although the dipole–dipole interactions among dots add to the anisotropy, they are too weak compared to the internal anisotropy. As a result, the nanodot exhibits a more-or-less soft magnetic behavior, similar to an unstrained, bulk CFO single crystal, which displays a cubic-like crystalline anisotropy and slim loops in both in-plane and perpendicular orientations. \[27\]

2.3. Epitaxial CFO Nanodot Array and Complex Magnetic Domains

For CFO nanodots, it is a challenging, although meaningful, task to directly deposit large-area epitaxial structures, which to the best of our knowledge has not been reported so far. By optimizing the deposition parameters, we were able to achieve an epitaxial nanodot array directly from deposition. Taking advantage of the large area (10 x 10 cm²) fabrication potential, we were able to fabricate and characterize the structure by X-ray diffraction (XRD). Figure 7a shows the XRD pattern for the nanodot array. The CFO (004) and (008) peaks

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Figure 2. a) AAO mask on SRO/STO substrate. Inset: magnified image showing the ordered pores. b) CFO nanodot array together with a partially removed AAO mask. The image was obtained by tilting the sample by 45° in order to visualize the cross-section of the mask. c) Well-ordered CFO nanodot array. d) Size distribution of the CFO dots. Insets: Pair distribution function (PDF, left inset) and FFT (right inset) derived from the SEM image of a dot array showing the nearly hexagonally ordered structure.

Figure 3. Cross-section TEM images of CFO dots. a) CFO dot array along with the detached AAO mask. b) EDX spectrum for a dot on a substrate to show its elemental composition. c) HRTEM of a CFO dot. Insets are the FFT pattern. d) Magnified high-resolution lattice image from (c).
can be identified although the peak intensity is rather weak. The epitaxial relation was confirmed by a Φ-scan (Fig. 7c), which shows four sharp peaks, indicating a cubic-on-cubic epitaxial growth of CFO on STO. The (004) rocking curve (Fig. 7b) shows a narrow full-width-at-half-maximum (FWHM) of 0.3°, indicating a good epitaxial quality. The epitaxial state could further be confirmed by the reciprocal space mapping along the STO(002) plane, in which the CFO(004) diffraction spot can be indentified in spite of its weak intensity, further confirming its high-quality epitaxial nature (Fig. 7d). The CFO diffraction spot shows a more-or-less symmetric shape and is centered at $q = 0$, suggesting a good cubic-on-cubic epitaxial growth for the film on the substrate plane without a detectable tilting.

The magnetization of the CFO nanodots was further studied by MFM micrographs, as shown in Figure 8. To obtain the remanent states of the CFO dots (diameter: ~290 nm, height: ~80 nm), we premagnetized the nanodots by a field perpendicular to the substrate surface before imaging the MFM micrographs, and then a reversed field was applied to further examine the switching of the magnetic states. As shown in Figure 8b, the MFM micrographs of the dots after the initial magnetization do not show uniform single-domain states like the ones in Figure 5f, but rather exhibit a dark–bright contrast inside the dots, indicating a multidomain structure. As the area of the dark region is larger than that of the bright region for most dots, a net magnetization can be expected. After applying a reversed field (Fig. 8d), the dark–bright contrasts have changed, but the dots still have a complex domain structure.

To further understand the magnetic states, the MFM micrographs of some typical domain states were recorded and are shown in Figure 8e. Based on the contrast of the MFM images, we could identify the spin configurations for the dots (considering only the...
we were able to achieve uniform single domains (Supporting Information, Fig. S1).

The observation of bubble and other complex domains in epitaxial spinel oxide nanodots are interesting both from fundamental research and application viewpoints. It paves the way to further investigate the micromagnetization inside nanostructures and control the spin states through strain and possible magnetoelastic effects. It also creates opportunities for device applications like memories, as bubble domains are rather stable against disturbance compared to single domains. Furthermore, the direct growth of epitaxial nanostructures is promising for designing more complicated dot array structures, for example, multilayer spin filters for either device applications or fundamental research.

3. Conclusions

Well-ordered CFO nanodot arrays were successfully fabricated by a combination of PLD and ultra-thin self-organized AAO masks. The dot size was varied from 35 to 300 nm and the interdot distance from 60 to 500 nm. These dots show slim magnetization hysteresis loops and a unique temperature-dependent magnetic behavior. MFM images indicate a cluster-like magnetic behavior from the dipole–dipole interaction between small dots (diameter ~60 nm) and more-or-less individual magnetic behavior for larger dots (diameter ~300 nm). Finally, by optimizing the deposition parameters, we were able to obtain epitaxial dot arrays, as confirmed by XRD Ψ-scans and reciprocal space mappings. The epitaxial dots demonstrate complex multidomain structures such as bubble domains or stripe domains due to the large demagnetization inside the dots.

4. Experimental

Fabrication of Nanodot Arrays: The fabrication procedure is schematically illustrated in the flow chart of Figure 1a. A conducting layer of SRO was deposited on single-crystalline substrates of STO or MgO by PLD for the purpose of a better adhesion and control of the magnetic properties (i). Ultrathin AAO masks with self-ordered arrays of pores with various pore sizes and pitches were prepared by an anodizing technique as described elsewhere [21,22]. The ultrathin AAO mask was then transferred onto the substrate (ii). Subsequently the CFO was deposited through the mask by PLD in an ambient pressure from 10 \(^{-5}\) bar to 0.05 mbar at elevated temperatures ranging from 200 to 550 °C (iii). Finally, the AAO mask was mechanically removed to obtain extended arrays of CFO nanodots (iv).

Instruments: The crystal structure was characterized by XRD θ–2θ scans using a Philips X’Pert MRD diffractometer with CuKα radiation. Magnetic properties were characterized by SQUID magnetometry and MFM (SPM, DI 5000) with a tip-height range of 50–100 nm. SEM images were obtained by a JEOL JSM-6300F microscope. TEM investigations were conducted by a Philips CM20T (Philips, Netherlands) at a voltage of 200 kV and a HRTEM JEOL 4010 (JEOL, Japan) at 400 kV. The samples for TEM were thinned using mechanical and ion-beam-based standard methods.
Cylindrical bidomain state (vi).

(ii), decentered bubble domain (iii), stripe domain (iv), single domain state (v), and hemicylindrical bidomain state are demonstrated: bubble domain (i), reversed bubble domain (b) and (d) and their corresponding schematic spin configurations are shown in (e), in which a magnetic states (c,d). Enlarged MFM images of various spin states that are picked up from –H surface (a,b) and switched by a reversed magnetic field (diameter: 290 nm, height: 80 nm) that are premagnetized by a field (H) perpendicular to the surface (a,b) and switched by a reversed magnetic field (−H) to investigate the switching of the magnetic states (c,d). Enlarged MFM images of various spin states that are picked up from (b) and (d) and their corresponding schematic spin configurations are shown in (e), in which a range of domain states are demonstrated: bubble domain (i), reversed bubble domain (ii), decentered bubble domain (iii), stripe domain (iv), single domain state (v), and hemicylindrical bidomain state (vi).

Figure 8. AFM topography images (a,c) and MFM micrographs (b,d) for epitaxial CFO dots (diameter: ~290 nm, height: ~80 nm) that are premagnetized by a field (H) perpendicular to the surface (a,b) and switched by a reversed magnetic field (−H) to investigate the switching of the magnetic states (c,d). Enlarged MFM images of various spin states that are picked up from (b) and (d) and their corresponding schematic spin configurations are shown in (e), in which a range of domain states are demonstrated: bubble domain (i), reversed bubble domain (ii), decentered bubble domain (iii), stripe domain (iv), single domain state (v), and hemicylindrical bidomain state (vi).

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