Fabrication of Large-Area Ferromagnetic Arrays Using Etched Nanosphere Lithography

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Nanosphere lithography (NSL) is a simple, cost-effective, and powerful technique capable of producing large-area arrays of ferromagnetic nanostructures with dimensions below 100 nm. These properties make NSL an attractive process for the fabrication of arrays of magnetic elements with applications in magnetic data storage. The main disadvantage with conventional NSL is that the monolayer of spheres always contains imperfections that are transferred to the resulting nanostructures. This can significantly affect the structural and magnetic properties of the fabricated array. In this paper we present a novel adaptation of NSL that reduces the effect of such defects on the resulting nanostructures. The technique also offers excellent control over the diameter, aspect ratio, and pitch of the fabricated elements. These properties are demonstrated through the fabrication of arrays of Ni elements of 210 nm diameter and arrays of Co elements with diameters between 200 and 320 nm.

1. Introduction

Self-assembled and patterned magnetic nanostructures are currently the subject of much interest due to their enormous potential in future nanotechnology. High-density magnetic recording is one area where a move toward the use of patterned media promises to increase storage densities by several orders of magnitude compared to that currently available in magnetic disk drives. In these systems nanofabrication or self-assembly techniques are used to produce artificially isolated elements of magnetic material, typically of dimensions below 100 nm. Each artificially fabricated magnetic element in the pattern has the properties of a single domain particle with only two possible magnetic states, “up” or “down”, corresponding to those of a recorded bit, “1” or “0”. Given the low dimensions and high anisotropy, the overall density of information which can be achieved is estimated to be well above 1 Tbit/in.².¹

Although the advantages of using patterned recording media are evident, the mass production of these systems for both commercial and research purposes is complicated due to the cost and time scales involved in fabrication. For instance, a typical fabrication process of a patterned array would involve electron-beam lithography (EBL). EBL can achieve very high resolution, down to 5 nm/feature. However, the area of the pattern is unlikely to exceed an area of 1 mm², which is insufficient for application as a recording medium. Even with the possibility of replicating the pattern over a larger area,² this method is not yet sufficiently fast and reliable. The limited area of patterns has also presented problems with regard to the application of magnetic and structural characterization techniques. The limitation in the overall volume of magnetic material directly relates to the maximum amplitude, which can be obtained from measurements. With the samples available from EBL, many standard magnetization techniques are simply not sensitive enough to resolve the signals. In this sense the main problems in the fabrication of patterned recording media still remain: finding a fast and cost-effective process, capable of producing patterns over a large area and with high resolution.

Nanosphere lithography (NSL) is a simple and very effective technique, which fulfills the above criteria³ and is thus valuable for producing prototype patterned media samples. In a typical procedure, fabrication of samples is achieved by depositing a single layer of polystyrene (PS) spheres from a colloidal suspension. Under correct conditions, evaporation of the solvent causes the spheres to form an ordered monolayer at the sample’s surface. The monolayer can then be used as a matrix for metal deposition. After metal deposition and removal of the spheres, a pattern of sub-micrometer-size particles is achieved.⁴ Commercial availability of nanospheres with diameters from 50 nm to greater than 1 μm makes it possible to vary the size and pitch of the magnetic elements.

However, one of the main problems associated with this method is that the monolayer of spheres always contains dislocations resulting in agglomerations of particles after metal evaporation.

In this paper, we suggest a method which not only avoids agglomerations but also improves control over the dimensions of the fabricated elements. This method follows the approach described previously by Haginoya et al.,⁵ where a monolayer of PS spheres is used to create an array of holes. We have extended this idea by developing a technique that allows electrodeposition of ferromagnetic material into the array of holes and offers control over the size and aspect ratio of the resulting elements. Below it is demonstrated that using this fabrication process, one can produce patterned, magnetic arrays, over an area greater than 1 cm², with the diameter of a single element in the range of 100 nm to 1 μm. Although this technique is not suggested as a commercial method for the production of patterned media, it provides an ideal basis for studies...
The base pressure was 10⁻³ mTorr and an Ar ion pressure of 5 mTorr then deposited on top of the metallic layer using RF sputtering. It was found, however, that SiO₂ samples were placed in an ultrasonic bath, first in alcohol and then in Milli-Q water before being thoroughly dried. This ensures the close-packed monolayer. It should be noted that using conventional methods, it is necessary to carry out surface treatments to make the substrate hydrophilic before depositing the PS spheres. This ensures that the Ni elements have near-vertical sidewalls and an aspect ratio of close to 1.

After sphere deposition, the samples were dried in an enclosed atmosphere at 55 °C for approximately 20 min. Large monolayers formed, typically of areas greater than 1 cm². The monolayers were identifiable by their characteristic, colored interference fringes, visible when illuminated with polychromatic light. To obtain elements of various diameters, the sizes of the PS spheres were reduced after deposition. This was achieved by RIE in an O₂ atmosphere. A pressure of 90 mTorr and an O₂ flow rate of ~2.00 cm³ s⁻¹ were used along with a range of etching times. Earlier work done by Huginoya et al. indicated that the sphere diameter can be related to the etching time by the expression,

\[ d = d_0 \cos(kt/2d_0) \]

where \( d \) is the diameter of the spheres after an etching time \( t \), \( d_0 \) is the initial diameter, and \( k \) is a constant dependent on the etching conditions.

After RIE, a 50 nm layer of MgF₂ was evaporated onto the samples, covering the spheres and filling the recesses between them (Figure 1b). Removal of the spheres was achieved using alcohol in an ultrasonic bath, resulting in an array of holes in the MgF₂ layer. As SiO₂ is etched preferentially to MgF₂ in a CHF₃ atmosphere, the MgF₂ acts as an etch mask for transfer of the pattern into the SiO₂. The etching process was continued for sufficient time to transfer the pattern completely through the SiO₂ layer, reaching the metallic electrode below (Figure 1c). Finally, magnetic elements were grown by electrodeposition in either a nickel sulfamate or a cobalt sulfate bath (Figure 1d). The deposition was carried out at a current density of 250 mA cm⁻², a temperature of 50 °C, and pH 5.0.

3. Results

Scanning electron microscopy (SEM) was used to investigate the structural properties of the fabricated arrays. Figure 2 shows a close-packed array of holes with an average diameter of 210 nm embedded in a MgF₂/SiO₂ matrix. The holes show excellent edge definition and a good degree of short-range order. There are some variations in the diameter of the holes which are thought to be due to a combination of nonuniformity in the RIE process and polydispersity of the PS spheres.

Figure 3 shows an array of 210 nm diameter Ni elements after transferral of the pattern through the SiO₂ layer and subsequent electrodeposition. The array shows good height uniformity with no overplating and very few unfilled holes. The cross-sectional image (Figure 3c) shows that the Ni elements have near-vertical sidewalls and an aspect ratio of close to 1.

To demonstrate the flexibility of the technique, we have also produced arrays of Co pillars of height ~ 250 nm and element diameters of 320, 240, and 200 nm. This range of diameters was produced by etching the spheres in an O₂ atmosphere for 30, 90, and 120 s, respectively.
SEM images of two such arrays are shown in Figure 4. The Co and Ni arrays both exhibit similar structural properties.

The arrays may be characterized by two types of order, long-range and short-range. When viewed at low magnification, differently oriented domains are visible much like the grains seen in polycrystalline atomic structures, with little correlation between them. Within individual domains, however, the elements are clearly ordered. Although imperfections such as vacancies may still be present, the positions of adjacent elements are strongly correlated. Domains with a single orientation have been obtained over areas of up to 15 mm², but these contain dislocations in their crystal structure. Well-ordered grains with only minor packing errors are typically of an area of 1600 μm².

A quantitative analysis of the array geometry within the grains was achieved by the application of a 2D modulus Fourier transform to a low-magnification SEM image. An image of a single grain of an area of 400 μm² (~3000 elements), containing holes formed by a monolayer of 390 nm spheres was used for the transform. The inset of Figure 4 shows the Fourier image of the array, which clearly demonstrates the hexagonal lattice structure. The distance between the centers of adjacent elements in the array can be extracted from the distance between adjacent peaks in the Fourier image, yielding a value of 376 nm. This is within 3.6% of the original average sphere diameter of 390 nm, highlighting the close-packed structure of the monolayer. The difference between the two values is likely caused by a combination of the size distribution of the spheres and the finite uncertainty in the original image size used for the transform.

To confirm that the arrays exhibit magnetic properties, longitudinal magneto-optical Kerr effect (MOKE) measurements were performed. A HeNe laser was used as an s-polarized light source, and a magnetic field was applied in the plane of the sample. Figure 5 shows the hysteresis loop obtained for the Co array of 320 nm diameter nanomagnets. The hysteretic behavior confirms that the electrodeposited elements behave ferromagnetically, with an in-plane remanence of ~0.4 and a coercivity of ~260 Oe.
4. Discussion

Despite the possible advantages of NSL in terms of speed, cost, and simplicity, there are also a number of well-documented problems. These include vacancies, dislocations, and small polycrystalline domains. In a typical NSL process, an array of spheres is used as a direct mask through which material is evaporated producing a “honeycomb” array of particles. This presents a range of problems in terms of the production and characterization of magnetic nanostructures. First, agglomerations of magnetic material accumulate at lattice defect sites. These agglomerations can dominate the magnetic properties when bulk measurements are made, limiting magnetic characterization to local techniques such as magnetic force microscopy (MFM). Second, the method is restricted to the production of triangular elements in a honeycomb array. Figure 6 shows an array of nanospheres deposited on SiO₂ and the resulting array of magnetic particles exhibiting these features.

Using etched NSL, imperfections in the nanosphere array still exist, but their effects on the magnetic properties of the sample are negated because the spheres are not used as a direct mask for deposition. This avoids agglomerations of magnetic material allowing accurate characterization using conventional bulk methods such as vibrating sample magnetometry (VSM). Perhaps the most valuable feature of the technique is the control afforded over the dimensions of the array. For magnetic storage applications there are three parameters that are of critical importance and hence merit careful study. First, the pitch is important as this affects the density of data that can be stored. Second, the diameter of each element will affect the strength of the interactions in an array and the thermal stability of stored data. Third, the aspect ratio of individual elements controls the strength and direction of the shape anisotropy which may be used to define media as “perpendicular” or “longitudinal.” Etched NSL allows control over all these features via the following: the size of the nanospheres used to form the monolayer controls the pitch, the sphere etching time controls the element diameter, and the thickness of the sputtered SiO₂ layer controls the aspect ratio. The method is thus ideally suited to the fabrication and systematic characterization of samples with a range of dimensions.

For use in magnetic data storage, element diameters of well below 100 nm are required to achieve sufficient areal densities. Theoretically, the RIE time of the spheres can be increased indefinitely to produce arbitrarily small particles. In practice, however, it is expected that due to nonuniform etching of the PS spheres, edge roughness will become significant for diameters below 100 nm, leading to an appreciable effect on magnetic properties. This may be overcome by using smaller diameter spheres in the formation of the original monolayer mask. For example, a monolayer could be deposited using spheres of initial diameter of 200 nm. A mask of these dimensions would require considerably less etching time to obtain diameters below 100 nm, and hence the edge roughness would be reduced. However, our initial experiments have found that although it is possible to produce monolayers using 200 nm spheres, the correlation length of such samples is reduced and the monolayers consist of a number of relatively small grains. As the sphere diameter becomes comparable to the thickness of the MgF₂ mask, further steps would also be required in the lithography process to aid sphere removal.

In this study, electrodeposition is used as a convenient mechanism for depositing magnetic material through a
dielectric mask. Studies\(^2,16\) have also shown that electrodeposited structures are capable of supporting the two stable magnetization states required for binary data storage. However, it is envisaged that this technique could be adapted to allow evaporation or sputtering of magnetic material and subsequent lift-off as an alternative. This would reduce the number of steps in the fabrication process and increase the range of materials that could be deposited. In a lift-off process, SiO\(_2\) substrates could be used directly, without the need for evaporation of a metal electrode layer or additional sputtering of SiO\(_2\).

5. Conclusions

We have demonstrated a method of producing size-tunable arrays of magnetic nanostructures using a novel adaptation of NSL. The fabrication process combines the benefits of NSL, including simplicity, low cost, high throughput, and fabrication over large areas, while avoiding the agglomerations of magnetic material and restricted geometry associated with the conventional technique. The fabrication process also allows control over the pitch, diameter, and aspect ratio of the patterned array. These attributes constitute a valuable tool in the production of patterned magnetic arrays for studies of nanoscale magnetic properties and systematic characterization.

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