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Nanomagnetic Structures: Fabrication and Interactions

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ABSTRACT

Magnetic nanostructures with desirable properties such as monodispersed size and
crystallographic texturing can be fabricated by a number of synthetic techniques. In this paper,
we discuss methods for creating nanoclusters with fine control of individual properties and
their interactions, as well as a promising chemical technique that provides control of several properties
simultaneously. Current and potential applications also will be addressed.

INTRODUCTION

Nanomagnetic clusters and structures are scientifically very interesting because of the
unique physical characteristics that arise at this size scale. To take advantage of these properties
in applications, it is important to be able to control properties of both the particles themselves, as
well as collections of particles. For example, in high-density recording, it is important for the
medium to have decoupled or weakly-interacting magnetic grains that are less than 10 nm in size
and have a very narrow size distribution. The requirement of narrow size distribution can be met
by creating particles with a gas aggregation cluster deposition system [1]. Crystallographic
texturing of clusters could be of great use in perpendicular magnetic recording and can readily be
done by multi-layer sputter deposition and annealing [2]. Depending on the choice of matrix, the
final goal of decoupled grains is achieved.

It is a difficult problem to simultaneously control all of these parameters. Chemical
synthesis by a hydrogen reduction technique has high potential for controlling over each of these
parameters, as well offering the ability to organize clusters in 2D arrays. In this paper, we will
discuss the deposition of uniform particles by gas aggregation and the creation of textured media
by sputtering and annealing. We will also discuss how hydrogen reduction of metal salts in
porous alumina templates can be utilized for each of the desired properties, as well as greater
control of strongly-interacting and weakly-interacting magnetic grains in the form of complex
structures and isolated grains.

NANOCLUSTER FABRICATION AND ORIENTATION

Monodisperse-nanocluster films

Formation of metal clusters by gas aggregation, in which metal atoms are evaporated or
sputtered into a cooled inert gas flow at relatively high pressure, has been established in several
laboratories in the last decade. By repeated collisions with the carrier gas, the supersaturated
metal vapor nucleates and forms clusters. The gas-aggregation methods have been applied
extensively to produce small clusters of metals such as zinc, copper, and silver. In some cases
this method was used in combination with a mass filter such as a quadruple or a time-of-flight
The metal vapor for the cluster source can be produced by either thermal evaporation or sputter discharge [3]. The advantages of the sputtering-based cluster source are: (1) it can produce a very large range of mean cluster sizes of 200 to 15000 atoms per cluster, (2) it has a high degree of ionization from 20% to 50%, depending on the target materials, and (3) a wide variety of elements and alloys can be used as source materials. Figure 1 shows an example of Fe clusters produced in such a system.

We have prepared FePt and CoPt nanoclusters which have the high-anisotropy L10 phase after annealing [1,4,5]. The cluster size was controlled in a range from 3 nm to 6 nm by adjusting the preparation parameters such as sputtering power, Ar-He gas flow, and gas pressure. Uniform cluster size distribution with standard deviation $\sigma/d < 0.1$ is obtained. The size distribution can be further improved by employing the mass selector. Figure 2 shows the TEM image of as-deposited FePt nanoclusters. The corresponding cluster size distribution from more than 200 clusters is also included. Spherical clusters with an average size of 5.3 nm that fit a Gaussian distribution (with standard deviation $\sigma = 0.46$ nm, $\sigma/d = 0.09$) were obtained with a sputtering power of 200 W and Ar/He gas flow of 400/200 sccm. High resolution TEM image reveals some faceting of the FePt clusters as shown in Figure 3. This enlarged FePt cluster image shows the lattice fringes, indicating the single-crystal structure.
Cluster-assembled films can be fabricated by either embedding these clusters in a matrix by co-deposition or a multilayer process. The ability of the deposition technique to independently control these parameters makes it ideal for systematic studies of magnetic clusters. Recent studies on FePt:Ag cluster films suggest that the addition of Ag can lower the L10 ordering temperature and increase the coercivity significantly, but the orientation of the L10 FePt clusters is random [5]. Magnetization reversal studies on FePt:C cluster films revealed that the thermal stability factor $K_u V^*/k_BT$ is higher than 100, annealing temperature is higher than 600°C, and the anisotropy constant $K_u$ is as high as $1.2 \times 10^7$ erg/cm³ [1].

**Figure 3.** HRTEM images of FePt clusters with faceting. Right: an enlarged cluster showing lattice fringes.

**Figure 4.** Preparation method of non-epitaxial growth L10-phase FePt:X nanocomposite films.

Cluster-assembled films can be fabricated by either embedding these clusters in a matrix by co-deposition or a multilayer process. The ability of the deposition technique to independently control these parameters makes it ideal for systematic studies of magnetic clusters. Recent studies on FePt:Ag cluster films suggest that the addition of Ag can lower the L10 ordering temperature and increase the coercivity significantly, but the orientation of the L10 FePt clusters is random [5]. Magnetization reversal studies on FePt:C cluster films revealed that the thermal stability factor $K_u V^*/k_BT$ is higher than 100, annealing temperature is higher than 600°C, and the anisotropy constant $K_u$ is as high as $1.2 \times 10^7$ erg/cm³ [1].

**(001) orientation of non-epitaxially grown L10 FePt:X films**

While further investigations are needed for L10 FePt cluster orientation, here we discuss an alternative method of preparing oriented L10 FePt nanocomposites, the non-epitaxial growth of oriented L10 FePt nanograins by multilayer deposition and annealing. Figure 4 shows the schematic initial and final structures of oriented L10 FePt:X (X = Ag, C, B₂O₃, etc.) films. FePt/X or Fe/Pt/X layers were deposited individually on Si wafers or glass substrates by magnetron sputtering at room temperature and then annealed in vacuum for 5 to 30 minutes at various temperatures. The as-deposited multilayers become nanocomposite films with L10-phase FePt grains embedded in a non-magnetic matrix. The orientation of the c axis of the L10-phase nanoparticles is strongly dependent on initial multilayering of Fe/Pt as well as dimensions of the Fe, Pt, and X individual layers [2,6,7].

Figure 5 shows the effect of Ag concentration on the orientation of L10 FePt:Ag nanocomposite films [7]. The Ag content was varied from 0 to 20 vol. %. All the films clearly show the (001) superlattice peak, indicating that the Ag content (matrix) has a relatively small effect on orientation.
Hysteresis loops for an L10 nanocomposite FePt:C film are shown in Figure 6. Inset are the XRD patterns of the same FePt:C film, with (001) and (002) peaks that indicate (001) orientation. The full width at half maximum (FWHM), obtained from the rocking curve of the (001) peak, is 1.68° confirming a high degree of (001) texturing. The loop shows perpendicular anisotropy with square shape in the perpendicular direction due to the enhanced preferential FePt L10 (001) texture. The perpendicular loop shows a large coercivity ($H_c = 6.2$ kOe) and high remanence ratio ($M_r/M_s = 0.9$). The nanostructure of nonepitaxially grown L10 FePt:C thin films was characterized by TEM [2]. The results show that FePt grains with uniform size less than 5 nm are embedded in the carbon matrix and appear to be isolated.

**NANOSTRUCTURE FORMATION IN ALUMINA TEMPLATES BY HYDROGEN REDUCTION**

Metal clusters also can be made by a hydrogen reduction technique in porous alumina channels [8–10]. Templates with an average pore size of 200 nm and a thickness of 50 µm are loaded with alcohol solutions of Fe(NO3)$_3$·9H$_2$O and H2PtCl6·6H2O by a pressure cell in an Fe:Pt ratio of 1:1. The system is then reduced in flowing hydrogen gas at various temperatures and for various times to create particles or other more complex structures.

Hydrogen reduction in porous templates represents a one-step FePt L10 cluster synthesizing...
technique, compared with the two-step process of solution synthesis [11,12] where first fcc FePt is created and then annealed for the transformation to the more favorable fct crystal structure. The use of porous alumina templates is preferable to other templates such as diblock-copolymers, track-etched polycarbon, porous silicon, and zeolite [13,14] in hydrogen reduction because it is resistant to organic and inorganic compounds, is stable at high temperature, and can easily be removed with an aqueous sodium hydroxide solution.

**FePt nanoclusters**

When a porous alumina film was loaded with a 1 M iron and platinum salt alcohol solution and heated to 900°C in hydrogen for 1 hour, FePt L10 ordered clusters were formed inside the pores. Figure 7 is the X-ray diffraction pattern of the corresponding sample. At this high treatment temperature, partial crystallization of the alumina matrix is observed.

Figure 8 is a TEM image of the FePt clusters inside the nanochannels of the template. Nearly spherical FePt nanoparticles were formed and their sizes range from 5 nm to 75 nm. The hysteresis loop of the corresponding FePt cluster assembly is shown in Figure 9, with a room temperature coercivity of 29.3 kOe. These experimental results demonstrate that this technique is a very effective approach for synthesizing L10 FePt clusters.

**Figure 7.** XRD pattern of hydrogen reduced iron nitrate and platinum chloride mixture in porous alumina films at 900°C for 1 hr.

**Figure 8.** TEM image of the FePt clusters inside the alumina film after hydrogen reduction at 900°C for 1 hr. The sample is crashed in mortar and dispersed in acetone.
When FePt clusters are annealed at high temperatures, their chemical ordering and coercivity are both very high. A serious problem caused by this high temperature processing is the agglomeration of adjacent clusters. It was found that this agglomeration was by heat-driven surface Fe and Pt diffusion. To minimize this problem, CVD is introduced to create a carbon barrier between the clusters. This will increase the activation energy for surface diffusion, and in turn, reduce the diffusion rate when heated at high temperatures.

The fabrication of FePt:C nanocomposites consists of the synthesis of FePt clusters at low temperature and the introduction of carbon by CVD [15]. After the synthesis of FePt clusters at 650°C for 1 hr, the flowing hydrogen was switched to high-purity nitrogen containing 3 vol % C2H2 at the same temperature for 30 min for the deposition of carbon. The C2H2 flow component was stopped at the end of the CVD process, while the flow of N2 was retained. The oven temperature was then increased to 900°C and kept constant for another 30 minutes in high-purity N2 before being cooled to room temperature.

Figure 10 shows the morphologies of the FePt:C composite released from porous templates under TEM. The mean cluster sizes were (a) 8.7 nm, (b) 29.9 nm, and (c) 8.8 nm. The data were extracted using log-normal fitting of the histogram of corresponding samples. This result indicates that the agglomeration of FePt clusters is effectively blocked by the introduction of carbon while heating at 900°C.

Since the introduction of carbon prohibits the excessive agglomeration of FePt clusters, and reduces the exchange interaction among clusters, the coercivities of FePt:C composites are
Figure 11. The dependence of coercivities on annealing temperatures for FePt cluster-assembly with and without carbon.

Due to the confinement in the nanochannels of the template, the resulting FePt:C composite has nanofiber-like morphology. The diameter of the nanochannels inside the alumina template can be tuned from 5 nm to several hundred nanometers. Different magnetic clusters can be introduced by the same experimental procedure described in this paper. In this sense, quasi-one-dimensional nanocomposites of carbon with different magnetic clusters can be produced. They are aligned and may find applications in magnetic nanotechnology.
Alignment of FePt nanoclusters

It has been demonstrated that FePt clusters capped with surfactants (for example, oleic acid) will form a suspension in hexane [11]. As a suspension, they may behave as a liquid under the influence of capillary action. When the FePt L1₀ cluster suspension is drop-cast onto porous alumina templates, the clusters enter the pores because of the capillary effect. An external magnetic field applied at the same time may align these clusters during assembly.

From the illustration of the alumina template shown in Figure 12, the barrier layer consists of a regular hexagonal array of hemispherical cells above the pores. This is a generally accepted prototype of a porous alumina template. By carefully controlling the anodization process and structure of the aluminum foil, two-step anodization can create similar structures [13].

The alumina templates with a highly-ordered pore array were made by a two-step anodization process in a 0.3 M aqueous solution of oxalic acid and at a bias of 40 V. The pores were widened by immersing the film in a 5% H₃PO₄ aqueous solution for 30 minutes [14]. FePt clusters were then produced by hydrogen reduction at 650°C for 5 minutes. The clusters were released by dissolving the alumina matrix and capped with both octadecanethiol and oleic acid. After proper chemical processing, the FePt clusters with average diameter of about 11 nm precipitated out and were dispersed in hexane for further assembly. Figure 13 is an MFM/AFM pair obtained on the open side of the pores after the FePt clusters were assembled under an external magnetic field. From this figure the average pore diameter is about 60 nm and clusters entered the pores to a depth that is undetectable by the scanning magnetic tip.

Figure 13. MFM and AFM images on the opening side of the pores after the assembly of FePt clusters under external magnetic field.

Figure 14. MFM and AFM images on the bottom of the pores after removing aluminum matrix.
Figure 14 is another pair of MFM/AFM images from the capped end of the pores after removing the aluminum matrix. This figure demonstrates clearly that the clusters reached the bottom cap of the pores and form an ordered magnetic pattern. In other words, the cluster assembly is effectively mediated by the highly ordered array of pores.

Magnetic measurement indicates that the ordered array is magnetically anisotropic. The coercivities measured parallel and perpendicular to the pores are 13.4 and 10.2 kOe respectively. This work demonstrates that the FePt clusters can be manipulated after their synthesis, rearranged into a desired pattern, and partially oriented.

FePt nanotubes

Magnetic nanotubes are very promising in applications such as magnetic recording, drug-delivery and spintronics [10, 16–18]. It has been noted that it is difficult to tune the magnetic properties of the structures with electrochemical methods [19]. This refers, in particular, to magnetic compounds, such as intermetallics and ferrimagnetic oxides used as soft and semi-hard magnets. In this section, we discuss nanotubes created by hydrogen reduction in porous alumina templates, particularly L10 FePt and Fe3O4.

Templates loaded with a mixture of H2PtCl6·6H2O and FeCl3·6H2O were heated in hydrogen for 1.5 h at 560°C and FePt nanotubes formed inside the pores of the template. Fe3O4 nanotubes form when pores are loaded with an alcohol solution of 65 wt. % Fe(NO3)3·9H2O and heated in air, followed by processing at 250°C for 2.5 hr in flowing hydrogen.

Figure 15 is an SEM micrograph showing the FePt tubes after slight etching. The white deformed donut shapes are FePt, indicating that close-packed nanotubes were formed inside the pores. A likely explanation for the somewhat asymmetrical cross section of the tube ends is that
the templates were mounted on a sample holder with pores horizontal. As a consequence, the liquid Fe and Pt chloride mixture near the pore openings may tend to flow out of the tubes and accumulate during heating in hydrogen before reduction.

Figure 16 (a) shows a TEM image of the FePt tube, encased in alumina, taken after etching for 50 min and dispersing in acetone. The chemical bond between the interface of the FePt alloy and the inner walls of the nanochannels allows the formation of nanotubes rather than clusters [20]. Figure 16 (b) shows two adjacent Fe₃O₄ nanotubes after removal of the alumina matrix.

Figure 17 shows room-temperature hysteresis loops of FePt (a) and Fe₃O₄ (b), measured by SQUID magnetometry parallel (solid lines) and perpendicular (dashed lines) to the tube axes. While sharing some basic characteristics of magnetic hysteresis loops, the two curves exhibit two striking differences. First, the coercivity of the FePt nanotubes is about 20.9 kOe, much larger than the Fe₃O₄ nanotube coercivity of 0.61 kOe. Second, the difference between the parallel and perpendicular curves is much more pronounced for the oxide tubes. Both features are related to the magnitudes of the magnetocrystalline anisotropy of the two compounds—about $6.6 \times 10^7$ erg/cm$^3$ for L1₀ FePt and $-1.1 \times 10^5$ erg/cm$^3$ for Fe₃O₄.

Magnetic nanotubes may provide magnetic field sources at the nanoscale for nanoelectromechanical system (NEMS) [21]. Halbach cylinders create a homogeneous cavity field which is, in general, larger than the saturation magnetization of the material. Similar configurations exist for higher-order fields, such as quadrupole fields [22]. If templates with an ordered pore structure were employed, ordered arrays of magnetic nanotubes could be fabricated for use as non-volatile memory [18].

SUMMARY

In this paper, we have demonstrated a variety of synthetic techniques used for controlling properties of nanoscale magnetic structures. Gas aggregation cluster deposition is a powerful technique for making monodisperse metal clusters. Crystallographic texturing of films can be achieved by multilayer sputtering followed by annealing. Hydrogen reduction of metal salts in porous alumina templates is a useful technique for controlling many of these properties simultaneously and making either isolated particles or structures that require strong interactions such as nanotubes.
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