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Ion Beam Stabilization of FePt Nanoparticle Arrays for Magnetic Storage Media

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ABSTRACT

We describe the use of ion beam induced crosslinking to harden the organic matrix material of self-assembled arrays of monodisperse (4 nm) FePt nanoparticles, providing diamondlike carbon barriers to inhibit agglomeration of the nanoparticles under heat treatment. Such stabilization is necessary for the particles to survive the >500°C annealing required for growth of the fct $L1_0$ phase of FePt, whose magnetic anisotropy is necessary for application of such arrays for high density perpendicular recording. Selective area irradiation of continuous nanoparticle coatings, using ion beams patterned over a full disk by stencil mask or with ion projection optics, followed by dissolution of the unexposed coating, is proposed as a means of fabricating extended bit patterns consisting of isolated "islands" of FePt nanoparticles, with characteristic dimensions of tens of nanometers.

INTRODUCTION

The magnetic disk drive industry has recently seen demonstrations of storage density exceeding 100 Gb/in^2, and it seeks to continue increasing that density without loss of device reliability or appreciable increase of manufacturing complexity and cost. This suggests the need for pre-patterned magnetic media, with nanometer-scale features. The attractive concept of self-assembled FePt nanoparticle arrays, as described by Sun *et al.* [1,2,3], would offer ordered patterns of magnetically isolated 4nm particles, provided that the assembly could retain its integrity during the >500°C heat treatment required for formation of the chemically ordered fct ferromagnetic phase of FePt, whose substantial magnetic anisotropy could be viable for perpendicular recording. However, at such temperatures, the organic matrix of the particles is not stable, and agglomeration of the particles may take place, degrading the initially tight distribution of particle sizes, and the integrity of the particle array. In this paper, we report some preliminary success of ion beam irradiation of the organic-embedded layer prior to heating, as a means of inhibiting this agglomeration and generating a stable, hard medium.

Since we have currently no viable technology for reading or writing single nanoparticles as independent bits, we also propose a way in which the ion-stabilized nanoparticle medium would lend itself to robust, full-disk patterning with bits consisting of isolated islands of FePt nanoparticles, having practically addressable dimensions up to tens of nanometers. Such patterning would represent a challenge for standard optical lithography, with its interference-

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limited spatial resolution. However, in this case, we would define the islands with a patterned projection ion beam – a robust process, capable of delivering high resolution at this scale, with manageable cost and throughput.

FePt Nanoparticle Media

Sun *et al.* have demonstrated a technique in which decomposition of iron pentacarbonyl (or reduction of iron chloride), concurrently with reduction of platinum acetylacetonate in the presence of oleic acid and oleyl amine leads to the formation of monodisperse nanoparticles of FePt (diameter 4 nm ± 5%), whose surfaces are decorated with organic ligands, which constitute a ~ 2nm isolating barrier, preventing agglomeration of the particles that would otherwise occur spontaneously at room temperature. Self-ordered planar arrays of the nanoparticles may be made by dip-coating a substrate in a solution of the particles in a suitable solvent. The resulting extended self-ordered arrays of FePt nanoparticles suggest the possibility of high density magnetic storage, each particle constituting its own single domain, and representing the state of one "bit" by its magnetization direction. FePt nanoparticles prepared in this way, however, are found to be in the chemically disordered fcc phase, which has negligible magnetic anisotropy. The chemically ordered $L1_0$ fct phase of FePt displays high magnetic anisotropy, suitable for perpendicular recording, arising from its inherent alternation of (001) planes of Fe and Pt atoms. In the case of continuous polycrystalline films, this phase is formed by heating the disordered fcc phase to > 500°C after deposition at low temperature, or by direct deposition at high temperature. Unfortunately, such heat treatment presents a serious problem when applied to nanoparticle FePt layers, due to the thermal degradation of the isolating organic barrier and consequent onset of agglomeration of nanoparticles [4].

Ion Beam Stabilization of Nanoparticles

In order to enable the necessary high temperature annealing of FePt nanoparticle coatings, we have ion beam irradiated the as-prepared coating that consists of FePt nanoparticles separated by organic ligands, prior to such heat treatments. The ion species and energy are chosen to optimize the crosslinking of the specific organic material, to form a hard, thermally stable diamondlike carbon (DLC) [5, 6, 7]. Such a DLC embedment should inhibit the agglomeration of the FePt particles at high temperatures, and it will also constitute a durable disk surface, protecting the FePt from oxidation or corrosion.

As a preliminary test of this concept, we have characterized and compared the effective particle sizes in FePt nanoparticle coatings (a) as deposited, (b) after annealing in N_2 for 5 minutes at 700°C, and (c) after ion beam irradiation, followed by annealing in N_2 for 5 minutes at 700°C. The irradiation conditions (700 keV N^+, dose of 2 x 10^{16} ions/cm^2), were chosen [5] to provide a high density of ionization within the organic layer, and relatively low collisional energy deposition – with the goal of causing substantial crosslinking yet little displacement degradation that would lead to graphitic carbon bonding. However, systematic optimization of radiation conditions remains to be done, and this was simply a test of principle.

Small angle neutron scattering (SANS) was used to determine the equivalent average diameter of the FePt particle clusters in each sample, as shown in Table I. According to these results, the ion beam processed sample clearly displayed much less agglomeration than the

equivalent non-irradiated sample, following the same heat treatment. We anticipate that further work to optimize the beam conditions can lead to complete suppression of this agglomeration.

In contrast to the SANS data, which identify the size of particles regardless of their homogeneity or extent of crystalline structure, X-ray diffraction (XRD) measurements [4,8] for the same samples yielded information about the crystallographic grain diameter, d, of the FePt assemblies. They also evaluated the effectiveness of annealing in producing chemical ordering of the FePt to form the $L1_0$ phase. The values of d obtained are shown in Table I. It is noted incidentally that the as-prepared particles are evidently not single grains, on average, and thus d is initially less than the "particle size" of 4 nm [8]. The results show, again, that particle agglomeration is inhibited in the irradiated sample. Of interest also are the values obtained for $S_{average}$ (the average chemical order parameter) and f_0, the volume fraction of the assembly that has become chemically ordered under annealing. They indicate that, after 700°C annealing for 5 minutes, formation of the $L1_0$ phase is far from complete, being less complete in the irradiated sample.

It remains for future experiments to explore whether optimally irradiated samples will withstand the longer (or higher temperature) heating needed for complete ordering of the $L1_0$ phase.

Table I. Agglomeration of 4-nm FePt nanoparticles under heat treatment. For each sample, the "equivalent particle diameter" was obtained from neutron scattering data, and an average crystallographic grain diameter was obtained independently from x-ray diffraction measurements. The chemical order parameter, and the chemically ordered fraction indicate incomplete ordering in both of the samples, even after annealing for 5 minutes at 700°C under nitrogen.

Sample	Equivalent Particle Diameter *(from SANS)*	Crystallographic Grain Diameter *(from XRD)*	Chemical Order Parameter $S_{average}$	Chemically Ordered Fraction f_0
As prepared	4.5 nm	2.5 nm	0.0	0.0
Annealed 700°C in N_2 5 min.	66.0 nm	15 nm	0.70 ± 0.05	0.83 ± 0.05
Ion Irradiated; then Annealed 700°C in N_2 5 min.	9.4 nm	10 nm	0.50 ± 0.05	0.56 ± 0.05

Nanoparticle "Islands": A Proposal

As a practical matter, creating the ideal self-assembled arrays of single nanoparticles, ordered with adequate coherence over a full disk, and then developing appropriate spatially sensitive sensors to read and write on them individually, seems remote at this time. However, a more realistic approach for storage densities >100 Gb/in^2 may lie in ion-beam patterned arrays or "islands" of nanoparticles, each island being defined as a feature on the scale of tens of nanometers [9]. All islands should then have uniform magnetic switching characteristics, each being composed of un-coupled single-domain nanoparticles of identical size.

The fabrication process is illustrated schematically in Figure 1, and it is intended to be robust, and readily compatible with standard manufacturing tools. The process steps are:

- The entire disk is dip-coated with a layer (or layers) of FePt nanoparticles, held in their organic embedment.
- An ion beam is patterned using a stencil mask, either in contact with the disk, or preferably producing a reduced image on the disk by means of an ion projection tool. The patterned beam is used to harden the exposed ("island") areas, in a single brief exposure for the entire disk.
- A solvent rinse is used to remove the particle coating everywhere except the patterned islands.
- The $L1_0$ FePt phase is grown by high temperature annealing in an inert ambient, during which the DLC embedment protects the integrity of the particles, and any disorder of FePt that may have been caused by the irradiation is annealed out.

The optical micrograph in Figure 2 shows portion of a coarse test pattern created in this fashion by irradiation of a FePt nanoparticle coating, using a silicon contact mask with arrays of 500-nm holes at various pitches [10]. In this case, 20 keV He^+ ions, with a dose of 2×10^{16}/cm^2, were used. A brief rinse in hexane then removed the un-irradiated coating, leaving the islands shown.

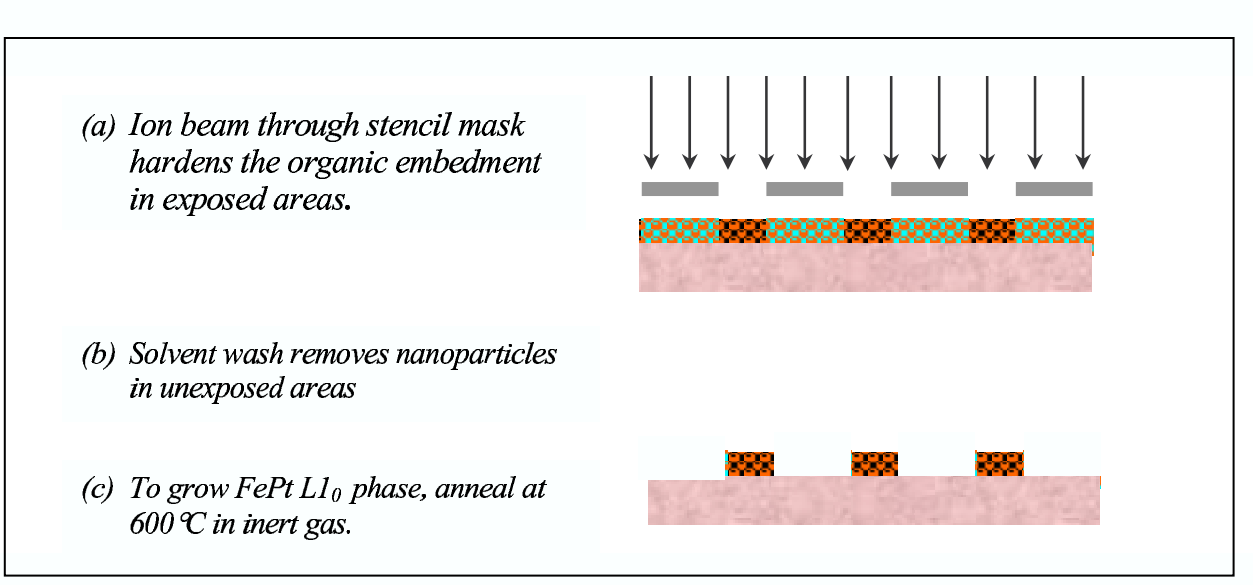

Figure 1. Process steps (schematically illustrated) for fabricating nanoparticle "island" features.

An ion beam projection system has recently been demonstrated [11,12 for magnetically patterning continuous multilayer $[Co\text{-}Pt]_n$ media. Its 45 keV Ar^+ ion beam, with 4× image reduction, was used to create a bit pattern typical for a 1-inch micro-disk, with feature resolution < 50 nm, and negligible aberrations or drift. In such a tool, because the mask can be so much larger than the pattern features, its production is straightforward, and it is robust and durable. The image reduction capability in a forthcoming version of this instrument is expected to be substantially greater still. Application of this tool for the full-disk patterning of islands of nanoparticles for continuous multilayer $[Co\text{-}Pt]_n$ media is expected to display similar or better spatial resolution.

The advantages anticipated in the "island" concept include

- Sharp edge definition for the features (not subject to the interference problems of optical lithography, or the limitations inherent in writing on continuous magnetic media).
- Small feature sizes are achievable.
- Uniformity of magnetic performance from bit to bit.
- A full disk pattern, (preferably via ion projection reduction) may be made in a single fast exposure, using robust masks.

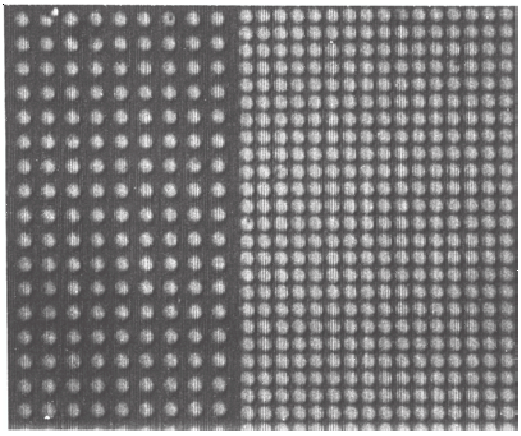

Figure 2. Coarse test pattern of hardened islands of FePt nanoparticles, (each island 500 nm diameter), at pitches of 800 nm and 1200 nm. The pattern was created by ion beam crosslinking of their oleic acid embedment in areas defined by a stencil mask in contact with the sample. The inter-island organic material was then removed by solvent rinse.

Nanoparticle Orientation

Before such nanoparticle coatings could be used as storage media, a means must be found for orienting the assembled particles with a common easy-axis direction. In the case of FePt, the high-anisotropy phase consists of alternating layers of Fe and Pt atoms, in (001) planes. Thus, in order to obtain a functional nanoparticle medium for perpendicular recording, we would need to produce assemblies of FePt nanoparticles whose (001) planes are all oriented parallel to the substrate surface.

How to achieve such common orientation of the nanoparticles is not clear. Some authors [13, 14] have reported limited success in radiation-assisted orientation of continuous polycrystalline films. However, we have so far been unsuccessful in such efforts. Further work to solve this problem is critical for this storage application of nanoparticle media.

SUMMARY

Ion beam stabilization of the organic matrix in FePt nanoparticle coatings has been shown to inhibit particle agglomeration during annealing, and is expected to provide additional physical protection of the recording medium. The extension of this technique to create patterned media consisting of high density arrays of nanoparticle islands appears to be feasible, and robust. The utility of the nanoparticle approach depends on development of a method for particle orientation. Work on these issues is proceeding.

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