Ferromagnetic Microdisks: Novel Magnetic Particles for Biomedical Applications

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ABSTRACT

In this report we propose a concept of magnetically soft disk-shaped particles with a number of properties useful for biomedical applications. The microdisks of permalloy (Py) Fe20-Ni80 alloy with diameter of 1 and 2 micrometers and variable thickness of 20 – 60 nm were fabricated using thin film sputtering techniques combined with electron-beam and optical lithography. The analysis of the experimental data and micromagnetic simulations shows that the magnetization reversal is accomplished via nucleation, displacement and annihilation of the magnetic vortex state. The disks demonstrate zero remanence and independent behavior of the assembly of disks, e.g. no agglomeration. A high magnetic moment equal to the saturation magnetization for the material can be achieved by applying a relatively small field. Furthermore, due to the collective resonant behavior of the spins, there are additional possibilities for the detection of the particles by using dynamic permeability measurements. The resonance frequency is found to be size dependent and can be tailored by choosing the appropriate geometrical aspect-ratio.

Keywords: magnetic nanoparticles, microfabrication, resonance, high frequency permeability.

1 INTRODUCTION

Biomagnetic technologies rely on the ability of biological substances to form supra-molecular structures when they are mixed with magnetic nanoparticles. The magnetic nature of the particle is used as a transduction mechanism for target-directed delivery, manipulation, detection and functional control of attached single bio-molecules or cells. Selective adhesion of the functional molecules is achieved by coating the magnetic particles with a special surface layer [1]. Major efforts have focused on magnetic particles prepared by standard aqueous precipitation techniques [2]. Typically, small particles of iron oxide are dispersed in, layered onto, or coated with a matrix to form beads ~1 μm in diameter. The challenge in this area is to achieve controllable growth of particles with desirable properties. The standard approach focuses on superparamagnetic nanoparticles for this application. For these particles, high magnetic fields are required to develop acceptable values of magnetization. As a result, these particles are generally difficult to detect and/or manipulate [3]. The intrinsic saturation magnetization M_s is typically small, however, using materials with a higher M_s result in only limited improvement because the magnetic content of the particle is only 10-20% of its volume. Larger, thus more magnetic, particles are more easily detected but they tend to agglomerate due to magnetic domain fringe fields, which limits their applicability. Here we will demonstrate how thin film growth techniques combined with traditional mask-transfer lithography can offer a new concept of magnetic nanoparticles with superior properties for bio-medical applications.

2 MICROFABRICATION

In this study, electron-beam lithographic patterning utilized a RAITH-150 system at 30 kV with a beam current of 100 pA. A bi-layer resist structure was used to facilitate the lift-off process. The PMGI resist [4] was used as a bottom layer, and ZEP520A [5] was used as an imaging (top) layer.

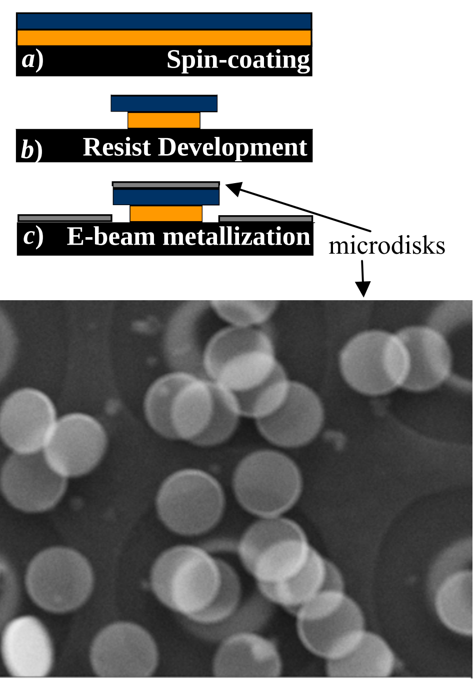

Figure 1: The microfabrication steps (top image) and Scanning Electron Microscope image of the fabricated microdisks (bottom image) with diameter of 1 μm, and thickness 40nm.

NSTI-Nanotech 2005, www.nsti.org, ISBN 0-9767985-0-6 Vol. 1, 2005

The silicon substrate was coated with the resists by spin casting at 5000 rpm, as schematically shown in Fig.1, step *a*). The sample was patterned in ring-shaped structures with inner diameter of 1 micrometer. After resist development (step *b),* the Permalloy (Fe20% - Ni80%) films were grown by d.c. magnetron sputtering (step *c*). The PMGI resist is more sensitive to the electron beam exposure dose, facilitating the lift-off process. The Scanning Electron Microscope image of particles with diameter of 1 micron and thickness of 40 nm detached from the substrate is shown in Fig. 1. The particles are virtually defect-free with perfect disk geometry. The process described here can be modified easily for low cost fabrication of large volumes of microdisks using optical or nanoimprint lithography.

3 MAGNETIC PROPERTIES

The static and dynamics properties of the fabricated samples were studied with micromagnetic modeling, magnetic force microscopy imaging, magnetization hysteresis loops and high frequency dynamic permeability measurements as described in the following sections.

3.1 Magnetization reversal

Figure 2 shows the hysteresis loop for an array of dots with thickness of 60nm and diameter of 2 microns measured using a SQUID magnetometer. The shape of hysteresis loops is typical for magnetization reversal due to nucleation, displacement and annihilation of magnetic vortices [6-10]. With decreasing field from the saturated state, the magnetization gradually decreases, showing an abrupt jump at the nucleation field H_n. At this field a single magnetic vortex is formed inside of each dot. This results in an important gain in magnetostatic energy.

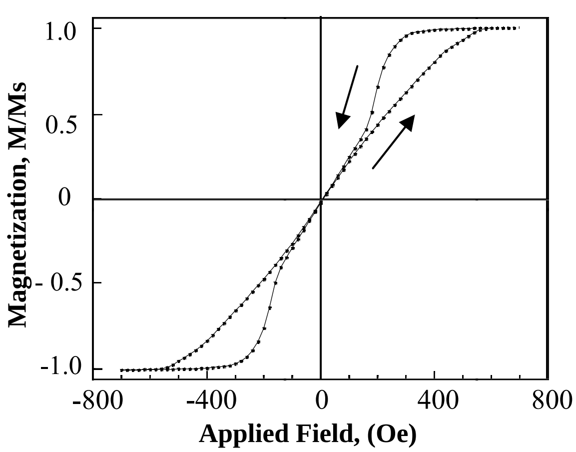

Figure 2: Magnetic hysteresis loop measured for disks with thickness of 60 nm and diameter 2 microns. The field is applied in the disk plane.

Magnetic Force Microscopy imaging (Fig. 3) confirms the presence of magnetic vortices through the detection of a stray field component perpendicular to the disk plane that is generated by a small (of order ~ 25 nm in diameter) vortex core in the center of each particle. This is in full agreement with micromagnetic modeling of the vortex spin distribution shown below.

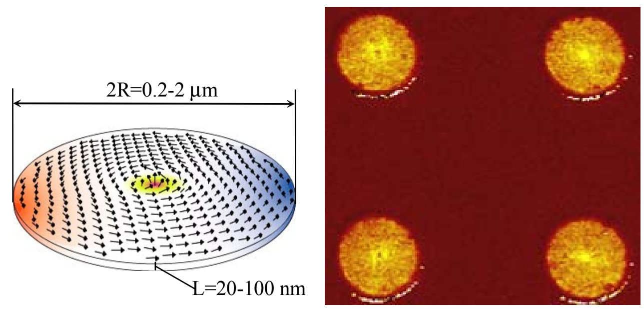

Figure 3: Micromagnetic model of the vortex (left) and Magnetic Force Microscopy images (right) reveal the presence of vortex cores in the center of each particle.

The linear part of the loops corresponds to the reversible vortex core displacement perpendicular to the applied field. When the applied magnetic field is equal to the annihilation field H_{an}, the vortex vanishes completely and the dot is stabilized again in the single-domain state. Both the nucleation and annihilation fields are size dependent.

The vortex annihilation field of a ferromagnetic disk, which is also the saturation field, can be estimated using the following equation [9]:

$$H_{an}(\beta, R, M_s) = \left[4\pi F_1(\beta) - \left(\frac{R_o}{R} \right)^2 \right] M_s , \qquad (1)$$

where R is the dot radius, $R_o = \sqrt{2A} / M_s$ is the micro-magnetic exchange length (~18 nm for Py), A is the exchange constant, L is the dot thickness, β=L/R is the geometrical aspect ratio of the disk, and $F_1(\beta) = \int_0^\infty dt\ f(\beta t) J_1^2(t)/t$ where $f(x) = 1 - (1 - \exp(-x))/x$ and $J_1(t)$ is the first-order Bessel function. These analytic predictions have been shown to agree well with micromagnetic simulations [9] and experiment [10], especially for small dot aspect ratios. The annihilation field can thus be controlled by varying not only the material parameters but also the geometry of the dot; H_{an} will decrease as a function of R, and increase with L and M_s. For disks fabricated with the lift-off technique, the annihilation field is typically a few kOe at most.

When the microdisks are suspended in liquid the external magnetic field will orient them parallel to the field direction. The magnitude the saturation magnetization that can be achieved by suppression of the vortex state is equal to the characteristic *Ms* of the material and can be as high as 1600 emu/cm^3 for Fe50%-Co50% alloy. For comparison, the M_s of most chemically synthesized nanoparticles is much smaller, for example, <100 emu/g [1].

3.2 Dynamics

To further demonstrate the unique properties of the ferromagnetic microdisks, we have examined the spin dynamics in this system. The spin excitations of the system may provide a useful means for detection. First, we have performed a set of micromagnetic calculations using a Landau-Lifshitz-Gilbert (LLG) solver [11]. Computational parameters are M_s= 860 emu/cm^3, the A = 1.3 × 10^{-6} erg/cm and a cell discretization size of 5 nm × 5 nm. To address the spin dynamics behavior, we first calculated the magnetization distribution under a small in-plane magnetic field of 100 Oe. This results in a displaced vortex spin structure with a small magnetic moment along the field (10% of M_s in this particular case). When the external filed is removed, the vortex returns to its equilibrium (remanent) state. This process is oscillatory nature with some damping, as shown in Fig 4 (upper plot). The period of the oscillations corresponds to an eigenfrequency of the system due to the translational motion of the vortex core.

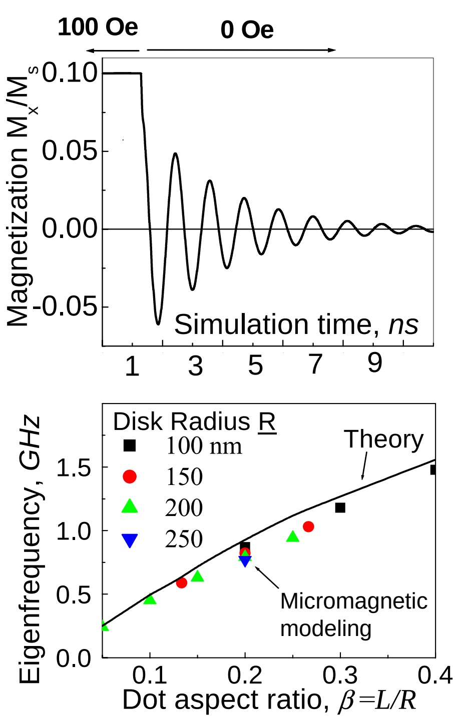

Figure 4: An example of magnetization oscillations of the magnetic vortex state when an external field is removed (upper plot) and the corresponding eigenfrequencies as a function of disk aspect-ratio (lower plot).

Repeating this numerical experiment for disks with difference sizes one finds that the frequency depends on both R and L. Surprisingly, the calculated eigenfrequencies for many different L and R, scale universally when plotted as a function of the disk aspect-ratio (Fig. 4, lower plot). The expected eigenfrequencies can also be predicted analytically [11, 12]. Based on a side-surface-charges-free vortex model, the frequency f_o of the vortex translational mode is given by:

$$f_o = \frac{\gamma}{2\pi} M_s \left[8\pi F_v(\beta) - \left(\frac{R_o}{R} \right)^2 \right], \qquad (2)$$

where γ is the gyromagnetic ratio ($\gamma/2\pi$ = 2.94 MHz/Oe for Py), $F_v(\beta) = \int_0^\infty dt t^{-1} f(\beta t) I^2(t)$ is a function of β, and $I(t) = \int_0^1 dx x J_1(tx)$. Therefore, the frequency can be predicted and adjusted if needed just by modifying R or L. Note that the sub-GHz frequencies calculated using Equation (2) agree very well with micromagnetic simulations.

To probe the dynamic properties experimentally we have prepared additional samples of 40 nm thick microdisks with diameters of 1 and 2 microns grown directly on top of microwave co-planar waveguides. The insert in Fig. 5 shows an optical micrograph of a portion of the 2 micron sample. There are ~1,200 disks on each waveguide. In this configuration the disks are electromagnetically coupled to a shorted thin film micro-strip transmission lines with a characteristic impedance of 50 ohms. An Aritsu vector network analyzer (frequency range: 40MHz to 20GHz) was used in the reflection mode to record the derivative of the real and the imaginary impedance as a function of frequency. Typically a 1 to 4 milliWatt drive signals was applied.

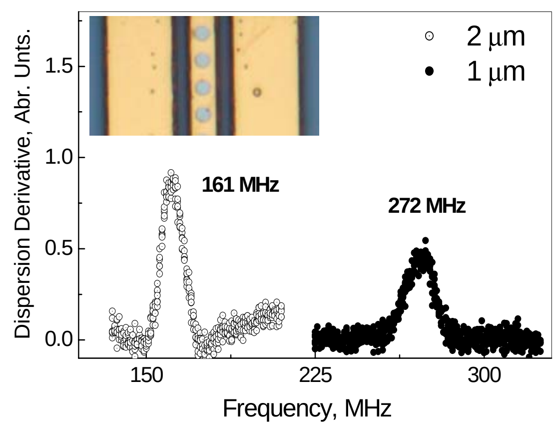

Figure 5: Frequency dependence of the dispersion derivative measured for 40 nm-thick microdisks, 1 and 2 microns in diameter, of Fe20%-Ni80% alloy. The detected resonance peaks at 161 and 272 MHz correspond to the eigenfrequency of the collective excitation of the spins predicted in micromagnetic simulations.

The experimental spectra for these two representative samples are shown in Fig 5. The S/N is about 20/1 after 160 averages for the 2 micron disks and about 5/1 for the 1 micron disks. Each spectrum takes about 5 minutes to obtain. The spectra have well defined resonance peaks. Their positions at 161 MHz and 272 MHz for the 2 micron and 1 micron disks, respectively, agree with the eigenfrequencies predicted in micromagnetic simulations. To the best of our knowledge this the first direct experimental observation of magnetic resonant absorption due to the internal vortex-like spin structure of the disks. It is clear from Fig. 5 that due to the collective resonant behavior of spins, there are additional possibilities to develop a novel method of real-time detection and/or counting of the particles by exploiting their resonant properties. In such a device the particles would be flowing through a measurements cell equipped with a coil connected to the vector network analyzer (VNA). The detection mechanism is based on the significant increase in radio frequency absorption at the frequencies of collective spin motion. Based on other experiments and the dynamic range of the VNA, we would expect detection sensitivity at the 10^{-5} areal fraction.

4 SUMMARY

In summary, we have demonstrated how thin film growth techniques combined with traditional mask-transfer lithography can be used to fabricate magnetic microdisks that posses a number of unique features that are especially valuable for biomedical applications [13]. The microdisks have zero remanence due to the formation of magnetic vortices, which dramatically reduces interaction effects and the possibility of agglomeration. A very high saturation magnetization can be achieved by applying relatively small magnetic fields. Furthermore, the properties of the microdisks can be tailored by choosing an appropriate geometrical aspect-ratio. Due to the collective resonant behavior of spins, there are additional possibilities for detection by using radio frequency susceptibility measurements. Finally, the geometry of the disk has two distinguishable surfaces, top and bottom, that can be coated with different metal layers (thin films) during the sputtering process. Therefore, one has the unique possibility of targeted delivery of two different types of bio-molecules at once. The test-experiments on performance of the delivery functions of the functionalized bio-compatible micro-disks "in-vivo" is in progress and will be reported separately.

ACKNOWLEDGEMENTS

K. B. thanks the Natural Sciences and Engineering Research Council (NSERC) of Canada for a fellowship. Work at Argonne was supported by the U.S. Department of Energy, BES Material Sciences under Contract No. W-31-109-ENG-38. We also thank Ralu Divan and Leo Ocola for support with microfabrication and Pierre Roy for stimulating discussions.

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