X-ray Studies of Magnetic Nanoparticle Assemblies

S. Anders,[a)] M. F. Toney, T. Thomson, J.-U. Thiele, and B. D. Terris

IBM Almaden Research Center, 650 Harry Road, San Jose, CA 95120

Shouheng Sun, and C. B. Murray

IBM T. J. Watson Research Center, Yorktown Heights, NY 10598

a)   Electronic mail: simone@almaden.ibm.com

Monodisperse FePt nanoparticles were prepared using high temperature solution phase synthesis. Polymer-mediated layer-by-layer growth leads to precise control of the particle self-assembly. The narrow particle size distribution ($\sigma \leq 5\%$) offers the potential for increased data storage density by utilizing a smaller mean particle size and ultimately storage of one bit per individual nanoparticle. We have studied self-assembled multilayers of magnetic FePt nanoparticles. The $L1_0$ phase of FePt has a very high magnetic anisotropy which allows the magnetization of particles of about 4 nm diameter to be thermally stable at room temperature. Magnetic measurements using vibrating sample magnetometer were combined with X-ray diffraction (XRD) and Near Edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy to study the annealed FePt nanoparticle assemblies and to optimize annealing conditions. NEXAFS spectra showed that a fraction of the iron in the as-deposited particles was oxidized, and this fraction was reduced by annealing in inert or reducing atmospheres. A very thin layer (<0.4 nm) of oxide surrounding the particle is sufficient to explain the observed spectra. Structural analysis using XRD showed that a minimum temperature of 450°C was required to start the formation of the ordered ferromagnetic phase. Annealing for longer times and at

higher temperatures led to higher coercivity and larger fraction of ordered phase but also to the onset of some agglomeration of the nanoparticles.

I. INTRODUCTION

FePt nanoparticles offer the potential for very high storage densities due to very narrow particle size distributions, with ultimately the possibility of storing one bit per particles corresponding to storage densities of 20 Tbits/in^2. Magnetic nanoparticles produced by solution-phase synthesis [1] show a very narrow particle size distribution ($\sigma \leq 5\%$), which can be deposited in mono- and multilayers with very precise control using polymer-mediated layer-by-layer deposition [2]. To obtain these high storage densities the particles need to be magnetically isolated and have high magnetocrystalline anisotropy. We have studied FePt nanoparticles, as bulk and thin film FePt in the chemically ordered $L1_0$ phase is known to have very high magnetocrystalline anisotropy up to 10^8 erg/cm^3 [3]. As synthesized, the particles are in the chemically disordered fcc phase and hence superparamagnetic at room temperature. They need to be annealed in inert or reducing atmosphere in order to be transformed into the chemically ordered $L1_0$ phase.

It has been observed that annealing can lead to particle agglomeration at high annealing temperatures [4, 5], and this effect has been used intentionally to form strongly exchange-coupled FePt nanoparticle assemblies for large energy product permanent magnetic materials [6]. However, in magnetic recording applications agglomeration is not desirable.

We have studied the onset of the $L1_0$ phase transformation at low annealing temperatures, and the correlation between magnetic, chemical, and structural properties of FePt nanoparticles in order to investigate the possibility of obtaining decoupled magnetic nanoparticles with a high degree of chemical ordering.

II. PARTICLE SYNTHESIS AND SELF-ASSEMBLY FORMATION

Monodisperse 4 nm FePt nanoparticles were synthesized by superhydride reduction of $FeCl_2$ and platinum acetylacetonate $Pt(acac)_2$ at elevated temperature in the presence of oleic acid, oleylamine and 1,2-hexadecanediol. The composition of the FePt particles was controlled by tuning the molar ratio of the metal precursors.

Well controlled 3 layer assemblies of the particles were formed on Si(110) substrates by a polymer-mediated layer-by-layer self assembly process that included alternatively absorbing a layer of polymer and nanoparticles onto a solid substrate via surface ligand exchange [2]. The assemblies were annealed for 30 min at temperatures between 400° and 580°C in an Argon/Hydrogen mixture (96%/4%).

III. NEAR EDGE X RAY ABSORPTION FINE STRUCTURE MEASUREMENTS

The chemical nature of the assemblies was studied using Near Edge Absorption Fine Structure (NEXAFS) Spectroscopy at the Fe L_3 and L_2 absorption edges in total electron yield mode [7]. The measurements were performed at beamline 7.3.1.1 of the Advanced Light Source equipped with a spherical grating monochromator giving an energy resolution of $E/\Delta E=1800$. The spectra analysis included subtraction of a linear

background and normalization to the reference beam intensity measured on a gold grid monitor. Figure 1 shows the Fe L-edge NEXAFS spectra of the samples annealed at different temperatures together with reference spectra for metallic Fe, Fe_3O_4, α–Fe_2O_3 and γ-Fe_2O_3. As observed previously [8] the Fe spectra show some oxidation of the iron. The spectrum of the 400°C annealed assembly can be simulated by a superposition of the Fe_3O_4 and γ–Fe_2O_3 spectra. The spectra for the higher temperature annealed assemblies can be simulated by a superposition of the Fe and Fe_3O_4 spectra with a fraction of metallic Fe that increases with annealing temperature. The chemical reduction of the iron oxide with increasing annealing temperature is indicated by the increase of the peak ratios A/B and C/D in Fig. 1. The changes are not very large above 450°C and the spectrum still contains a substantial contribution of the Fe_3O_4 (70%) after annealing at 580°C.

Note that the oxide to metal ratio averaged over the depth of the whole assembly is quite different from the metal and oxide contributions to the spectra. If we assume a metallic FePt core surrounded by an oxide shell, this shell will dominate the spectra because of the short electron escape depth that determines the probing depth of NEXAFS. Using electron escape depths of 10, 5, and 1.5 nm for carbon, iron oxide, and Fe metal, respectively, we estimated that a thin oxide shell of < 0.4 nm is sufficient to produce the contributions to the total spectra that we have observed. This shell thickness correlates to a Fe/Fe_3O_4 ratio of 50%/50% averaged over the whole particle. However, we cannot exclude the presence of other oxides and, e.g., we can alternatively obtain a relatively good fit to the data for a Fe and γ-Fe_2O_3 superposition with 50% contribution of γ-Fe_2O_3

to the spectrum for the 580°C annealed assembly. This would correspond to a 0.25 nm thin oxide shell giving 67% metallic Fe averaged over the whole particle.

IV. X RAY DIFFRACTION MEASUREMENTS

Specular X ray diffraction using synchrotron radiation was used to investigate the structural properties of the assemblies. The scans show a weak, broad (111) peak for the as-synthesized assembly that increases and narrows with annealing temperature. No superlattice peaks are present in the as-synthesized and 400°C annealed assemblies while for higher annealing temperatures superlattice peaks appear and grow in intensity with increased annealing temperature. From the ratios of the superlattice peaks to the fundamental peaks and from the width of the (111) peak, the order parameter S, the fraction of the ordered phase f_O, and the (111) coherence length $l_{(111)}$ were determined as described in [9]. Figure 2 shows these data as a function of annealing temperature.

We find that the order parameter, which measures the degree of order within the partially ordered phase (S), does not change much with temperature once ordering has occurred above 400°C and remains about 0.6 (± 0.1). The fraction of the partially ordered phase increases with annealing temperature and reaches 0.7 (± 0.05) at 580°C. Therefore the average order parameter which is the product of the order parameter and fraction of ordered phase increases with annealing temperature. The onset of order occurs at the same temperature as the appearance of a metallic contribution to the NEXAFS spectra. In addition we find an increase of the (111) coherence length indicating the onset of agglomeration. The (111) coherence length is characteristic of the average total particle

size either in the fcc or $L1_0$ phase or a mixed phase. It increases with annealing temperature and reaches up to 2-3 times the nominal particle diameter of 4 nm. There is no indication in the data of an ordered oxide phase.

V. MAGNETIC CHARACTERIZATION

The magnetic properties of the assemblies were determined using vibrating sample magnetometer (VSM). All measurements were performed at room temperature. Unannealed assemblies have no coercivity and very small moment density of about 8 emu/cm^3. The sample annealed at 400°C (that is not yet chemically ordered) has no coercivity at room temperature and only about a third of the magnetic moment density compared to the partially ordered assemblies. The moment density increases to about 100 emu/cm^3 and does not change much once partial ordering has occurred and the assemblies become ferromagnetic at room temperature. The onset of ferromagnetism correlates with the appearance of the metallic Fe contribution to the NEXAFS spectra. The moment density shown in Fig. 3 is averaged over the whole thin film. If we assume a full bulk moment density of 1140 emu/cm^3 for the fully ordered FePt nanoparticles and a fraction of ordered phase around 0.6, this corresponds to a packing density of 0.15 similar to the packing density that can be estimated from TEM images [4] for 4 nm particles, hexagonal assembly, and about 6 nm particle distance. The coercivity increases with annealing temperature up to 4.8 kOe for 580°C. The increase of the coercivity is likely due to both the increased fraction of the ordered phase and agglomeration. In-plane and perpendicular VSM hysteresis loops are almost identical indicating the 3-D

randomly oriented easy axis distribution of the particles and the small contribution of shape anisotropy.

VI.   CONCLUSIONS

We have studied the onset of chemical ordering due to annealing of FePt nanoparticle assemblies. It was found that much of the Fe in the as-synthesized particles is partially oxidized, and the degree of oxidation is chemically reduced with increasing annealing temperature. First indication of chemical ordering, as measured by XRD, was found for assemblies annealed at 450 °C. With increasing annealing temperatures the fraction of ordered phase increases, although the amount of chemical order within the ordered regions does not increase significantly.   This onset of ordering correlates with the appearance of a metallic contribution to the NEXAFS spectra. The moment density is very low for as-synthesized assemblies and increases with annealing temperature in the 400-450°C range after which it remains constant at about 100 emu/cm^3 averaged over the whole film thickness.

The application of these nanoparticle assemblies to magnetic storage will require particle assemblies with isolated (not agglomerated) particles with high anisotropy.   Further improvements are necessary to reduce the onset temperature for chemical ordering and avoid agglomeration.   In addition alignment of the easy axes of the nanoparticles is required.

REFERENCES

[1] S. Sun, C. B. Murray, D. Weller, L. Folks, and A. Moser, Science 287 (2000) 1989

[2] S. Sun, S. Anders, H. F. Hamann, J.-U. Thiele, J. E. E. Baglin, T. Thomson, E. Fullerton, C. B. Murray, and B. D. Terris, J. Am. Chem. Soc. **124**, 2884 (2002).

[3] D. Weller, A. Moder, L. Folks, M. E. Best, W. Lee, M. F. Toney, M. Schwickert, J.-U. Thiele, and M. F. Doerner, IEEE Trans. Magn. **36**, 10 (2000).

[4] Z. R. Dai. S. Sun, and Z. L. Wang, Nanolett. **1**, 443 (2001).

[5] J. W. Harrell, S. Wang, D. E. Nikles, and M. Chen, Appl. Phys. Lett. **79**, 4393 (2001).

[6] H. Zeng, S. Sun, T. S. Vedantam, J. P. Liu, Z.-R. Dai, and Z.-L. Wang, Appl. Phys. Lett. **80**, 2583 (2002).

[7] J. Stöhr, *NEXAFS Spectroscopy*, Springer, Berlin 1992.

[8] S. Anders, S. Sun, C. B. Murray, C. T. Rettner, M. E. Best, T. Thomson, M. Albrecht, J.-U. Thiele, E. E. Fullerton, and B. D. Terris, Microelectr. Engin. **61/62**, 569 (2002).

[9] A. Cebollada, R. F. C. Farrow, and M. F. Toney, in *Magnetic Nanostructures*, Ed. H. S. Nalva, American Scientific Publishers, 2002, p. 93.

CAPTIONS FOR FIGURES

Figure 1: Fe L-edge NEXAFS spectra of 3-layer assemblies of 4 nm FePt nanoparticles annealed at different temperatures together with reference spectra for metallic Fe, Fe_3O_4, α–Fe_2O_3, and γ-Fe_2O_3.

Figure 2: Order parameter in the chemically ordered regions S, fraction of the ordered phase f_O, average order parameter S_{ave} = S x f_O, and (111) coherence length $l_{(111)}$ of the assemblies as a function of annealing temperature.

Figure 3: Perpendicular VSM hysteresis loops for the assemblies annealed at different temperatures.

Legend:
- S
- fo
- Save
- I(111)

X-axis: temperature (°C) — 350, 400, 450, 500, 550, 600

Left Y-axis: S, f_o, and S_{ave} — 0, 0.2, 0.4, 0.6, 0.8, 1

Right Y-axis: $d_{(111)}$ in nm — 0, 2, 4, 6, 8, 10, 12