

# NEXAFS study of self-assembled FePt nanoparticles

S. Anders<sup>1\*</sup>, S. Sun<sup>2</sup>, C. B. Murray<sup>2</sup>, J.-U. Thiele<sup>1</sup>, M. F. Toney<sup>1</sup>, and B. D. Terris<sup>1</sup>

<sup>1</sup> IBM Almaden Research Center, 650 Harry Road, San Jose, CA 95120

<sup>2</sup> IBM T. J. Watson Research Center, Yorktown Heights, NY 10598

## INTRODUCTION

Over the past few years the storage density of magnetic disk drives has increased at a rate of greater than 100% annually. This increase was achieved by scaling the critical physical dimensions, however experiments and theory indicate that there is a limit to this scaling that will be reached within the next few years.

Today's magnetic storage media consist typically of quaternary alloys, e.g. CoCrPtB, with grain sizes in the range of 10-15 nm [1]. The magnetic anisotropy energy  $E$  per grain is given by the grain volume  $V_g$  and the anisotropy energy density  $K_u$  as  $E = K_u V_g$ . The thermal stability of the grain magnetization can be described by the stability ratio  $C = E / k_B T$  where  $k_B$  is Boltzmann's constant and  $T$  the temperature.  $C > 60$  [2, 3] is required to store information reliably for 10 years. If we assume cylindrical particles with a height of the typical film thickness of 20 nm and  $K_u$  of current media (about  $3 \times 10^5 \text{ J/m}^3$ ), this implies a minimum stable particle diameter of about 7nm for monodispersed particles.

Since ultimately the transition width is determined by the grain size, higher storage densities require smaller grains. Also, for constant signal to noise, it is desirable to keep the number of grains per bit constant, and thus the grain size is reduced as the density is increased. The grain size distribution for current granular media is very wide with a typical standard deviation for the grain diameter of about  $\sigma = 30\text{-}35\%$ . An increase in thermal stability and storage density and a reduction in noise can be achieved by reducing the median grain size with a simultaneous narrowing of the size distribution.

Magnetic nanoparticles [4] can have a very narrow particle size distribution. Here we describe the fabrication and study of magnetic nanoparticles films, and the requirements for their application to magnetic storage.

## SELF-ASSEMBLED LAYERS OF MAGNETIC NANOPARTICLES

A possible method to create new magnetic storage media is the deposition of self-assembled layers of magnetic nanoparticles [4] with a very narrow size distribution. In particular we have investigated FePt nanoparticles because the  $L1_0$  phase of FePt in thin film form is known to have very high magnetic anisotropy [5]. FePt nanoparticles were prepared by the combination of reduction of  $\text{Pt}(\text{acac})_2$  (acac=acetylacetonate) and thermal decomposition of  $\text{Fe}(\text{CO})_5$  or  $\text{FeCl}_2$  in the presence of oleic acid and oleyl amine. The nanoparticles can be easily dispersed in a variety of solvents. A drop of the solution is placed on the substrate and during the evaporation of the solvent a regular assembly of nanoparticles is formed. The elemental composition of FePt nanoparticle materials is tuned by varying the molar ratio of  $\text{Fe}(\text{CO})_5$  or  $\text{FeCl}_2$  and  $\text{Pt}(\text{acac})_2$ . The FePt particle size can be varied from 3 to 10nm by first growing 3nm monodisperse seed particles *in situ* and then adding more reagents to enlarge the existing seeds to the desired size. The size distribution of the particles is very narrow ( $\sigma \leq 5\%$ ) as can be seen in Figure 1 for a self-assembled layer of 6 nm particles.

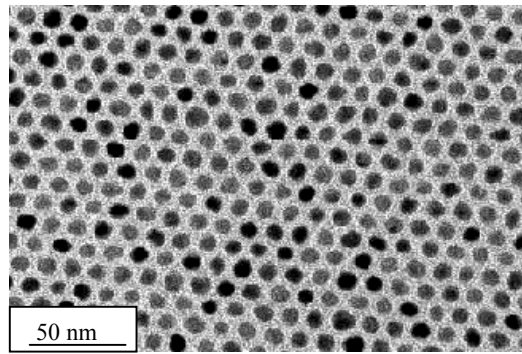


Figure 1: Transmission electron microscope image of self-assembled layer of 6 nm diameter FePt nanoparticles.

As deposited, the FePt nanoparticles are in the disordered fcc phase and are superparamagnetic at room temperature. Annealing at various temperatures and durations in nitrogen or forming gas transforms the particles to the ferromagnetic, ordered  $L1_0$  phase.

The coercivity of the annealed films typically increases with anneal time and temperature, and a minimum temperature of about 500°C is required to begin forming the ordered  $L1_0$  phase. An increased number of layers also leads to an increase in the film coercivity. For magnetic recording thin, high anisotropy layers of small nanoparticles are most desirable. The thinnest layers that showed coercivities  $> 300$  Oe (as measured by Vibrating Sample Magnetometer) were 1 layer films of 8 nm particles and 2 layer films of 4 nm particles. Superconducting quantum interference device (SQUID) measurements show that coercivities as high as 17 kOe can be achieved for 3 layer/4 nm particle thin films (deposited from  $\text{FeCl}_2$  and annealed at 800°C for 5 min. in  $\text{N}_2$ ). The easy axis of the particles is 3D randomly oriented, leading to identical hysteresis loops for in-plane and perpendicular measurements and a remanent magnetization  $M_r = 0.5 M_s$  where  $M_s$  is the saturation magnetization.

The chemical nature of the films was studied using near edge X-ray absorption fine structure spectroscopy (NEXAFS) measured in total electron yield at beamline 7.3.1. of the ALS. The data indicate that all films contain a substantial fraction of oxidized Fe. Figure 2 shows an example of the NEXAFS spectra for 1 and 7 layer films of 8 nm particles together with a metallic Fe reference spectrum. One can see that the 7 layer film shows a much more metallic character which is correlated to a much higher coercivity compared to the 1 layer film. The best fit to the experimental data is obtained for a weighted superposition of Fe and  $\text{Fe}_3\text{O}_4$  reference spectra (55%/45% for 1 layer and 75%/25% for 7 layers) but due to the similarity of the spectra of Fe and FeO and of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  we cannot exclude the presence of other oxidation states. The ratio of the contribution of metallic and oxidized iron to the spectra is not identical to the ratio of metallic and oxidized iron in the nanoparticles. We assume a geometry of the nanoparticles with a metallic FePt core surrounded by an oxide shell. The oxide shell will contribute more to the spectrum than the volume fraction of the Fe oxide because of the geometry and the short electron escape depth of only 2-5 nm. The assumption of a metallic core surrounded by an oxide shell is also supported by XRD results. For the 7 layer film of 8 nm particles it was found that 90% of the Fe is present in the ordered  $L1_0$  phase. A corresponding oxide shell of only 0.1-0.2 nm thickness is sufficient to produce a 25% contribution to the NEXAFS spectra.

Optimization of annealing conditions and chemistry led to a reduction of the oxidized Fe content and an increase in metallic Fe present in the ordered  $L1_0$  phase. Both correlate strongly with increase in the magnetic coercive field.

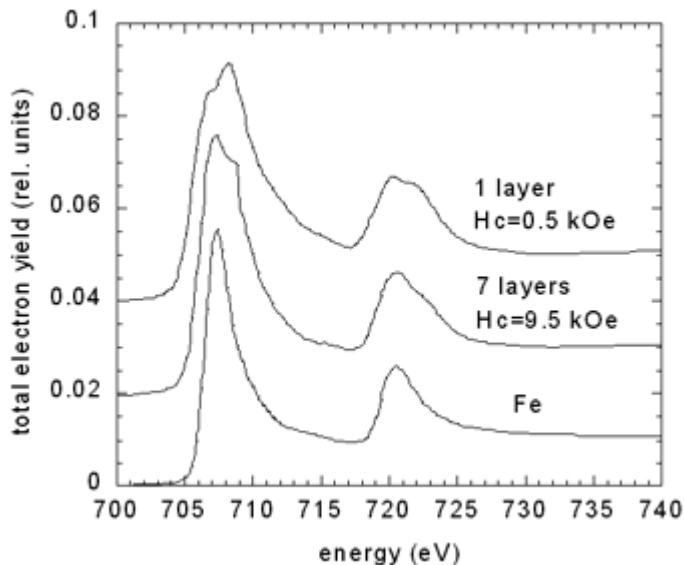


Figure 2: NEXAFS spectra for 1 and 7 layer films of 8 nm particles annealed at 580°C in N<sub>2</sub> for 30 min, together with a metallic Fe reference spectrum. The particles were prepared from FeCl<sub>2</sub>.

## CONCLUSIONS

Thin films of magnetic nanoparticles were investigated as potential candidates for high density magnetic storage media because they exhibit a very narrow size distribution and ultimately the potential of storing one bit per nanoparticle. NEXAFS showed that a fraction of the iron is oxidized, most likely in the form of Fe<sub>3</sub>O<sub>4</sub>. By optimizing the chemistry and anneal conditions we were able to produce very thin (1 layer/8 nm particles and 2 layers/4nm particles) ferromagnetic films with coercivities of > 300 Oe. Thicker films (3 layers/4nm particles) can have coercivities of up to 17 kOe. Further optimization is required to reach the goal of magnetic storage in the density range of 100 Gb/in<sup>2</sup> and above.

## ACKNOWLEDGMENTS

The authors would like to thank Andreas Scholl, Andrew Doran, and Hendrik Ohldag for their ongoing support of their work at the ALS. This work was supported by IBM.

## REFERENCES

- [1] Y. Kubota, L. Folks, and E. Marinero, *J. Appl. Phys.* 84 (1998) 6202-7.
- [2] S. H. Charap, P.-L. Lu, and Y. He, *IEEE Trans. Magn.* 33 (1997) 978-83.
- [3] D. Weller and A. Moser, *IEEE Trans. Magn.* 35 (1999) 4423-39.
- [4] S. Sun, C. B. Murray, D. Weller, L. Folks, and A. Moser, *Science* 287 (2000) 1989-92.
- [5] D. Weller, A. Moser, L. Folks, M.E. Best, W. Lee, M. Toney, M. Schwieckert, J.-U. Thiele, and M.F. Doerner, *IEEE Trans. Magn.* 36 (2000) 10-15.

Principal investigator: Simone Anders, IBM Almaden Research Center, 650 Harry Road, San Jose CA 95120.  
 Email: simone@almaden.ibm.com. Telephone: 408-927-2069.