# Thermal stability of self-assembled FePt nanoparticles[a)]

T. S. Vedantam and J. P. Liu[b)]
*Institute for Micromanufacturing, Louisiana Tech University, Ruston, Louisiana 71272*

H. Zeng[c)] and S. Sun
*IBM T. J. Watson Research Center, Yorktown Heights, New York 10598*

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We have produced self-assembled FePt nanoparticles by chemical synthesis and subsequent thermal annealing. The self-assembled samples were annealed in nitrogen or forming gas (95%Ar $+5\%H_2$) atmosphere for varying annealing time and temperatures. Thermal annealing above 500 °C resulted in phase transformation of the as-synthesized FePt from the chemically disordered fcc to chemically ordered fct structure which has a high uniaxial magneto-crystalline anisotropy. With increasing annealing temperature, the coercivity and the thermal stability factor $KV/kT$ were found to increase due to improved chemical ordering, irrespective of the annealing atmosphere. For samples annealed at 580 °C for 30 min in forming gas, the maximum coercivity obtained was 6.95 kOe. The samples annealed in forming gas showed higher coercivity and $KV/kT$ values than those annealed in nitrogen for the same annealing time and temperature. We have also measured the Curie temperatures of the FePt nanoparticle assemblies. The Curie temperatures were found to increase with increased annealing time for the samples annealed in nitrogen at 580 °C.  [DOI: 10.1063/1.1558233]

## I. INTRODUCTION

The rapid increase of areal density of magnetic recording requires media with smaller and smaller grain sizes. However, the magnetization of the very small grains becomes unstable due to the superparamagnetic effect.[1] A possible solution to overcome the problem of superparamagnetic effect associated with increasing areal density in current continuous media is to fundamentally change the way information is stored. Instead of having a fixed number of grains per bit, discrete single domain magnetic particles can be patterned onto a substrate such that each particle is capable of holding one bit of information. Such a media, known as patterned media,[2] will have very low noise caused by bit to bit transitions and help increase the areal recording density enormously. On the other hand, to enhance thermal stability of the medium, the magnetic material used should possess high magneto-crystalline anisotropy and high coercivity. The FePt-based nanoparticle arrays have been predicted to be excellent candidates for application in ultrahigh density magnetic recording because they are chemically stable and magnetically hard. The magneto-crystalline anisotropy is as high as $10^8$ ergs/cc in a fully ordered intermetallic phase.[3,4] This large crystalline anisotropy allows for thermally stable grain diameter down to 2.8 nm.[5] A self-organized magnetic array of FePt nanoparticles will contribute to an effort to design a magnetic medium capable of recording densities beyond 1 $Tb/in^2$.[1] The ultrahigh density recording potential of the FePt nanoparticles has stimulated great efforts in nanoparticle synthesis and assembly.[6] In this article, we report thermal stability studies on FePt nanoparticle assemblies produced by solution-phase synthesis and self-assembly, followed by thermal annealing.

## II. EXPERIMENT

The high-temperature solution phase decomposition of $Fe(CO)_5$ and reduction of $Pt(acac)_2$ was used to produce monodispersed FePt nanoparticles.[5,6] Deposition of the nanoparticle dispersion on a solid substrate and controlling solvent evaporation led to the FePt nanoparticle assemblies. Two sets of self-assembled samples were annealed at temperatures between 500 and 580 °C for annealing times ranging from 10 min to 2 h, in nitrogen and forming gas atmospheres, respectively. The heating rate applied was 20 °C/min and after annealing the samples were allowed to cool down at room temperature. The room temperature magnetic properties were studied by an alternating gradient magnetometer. The Curie temperatures were measured using a vibrating sample magnetometer.

## III. RESULTS AND DISCUSSION

The self-assembled FePt nanoparticles produced were 4 nm in diameter and they were uniformly distributed across the surface of the substrate. Thermal annealing above 500 °C converts the internal particle structure from chemically disordered face-centered cubic (fcc) phase to chemically ordered face-centered tetragonal (fct) phase which has high uniaxial magneto-crystalline anisotropy.[6] The degree of ordering depends strongly on annealing temperature. Annealing at higher temperatures leads to the evaporation/decomposition of the organic surfactant around each particle

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[a)]No proof corrections received from author prior to publication.
[b)]Author to whom correspondence should be addressed; present address: Department of Physics, UT Arlington, Arlington, TX 76019; electronic mail: pliu@uta.edu
[c)]Also affiliated with Institute for Micromanufacturing, Louisiana Tech University, Ruston, LA 71272.

 

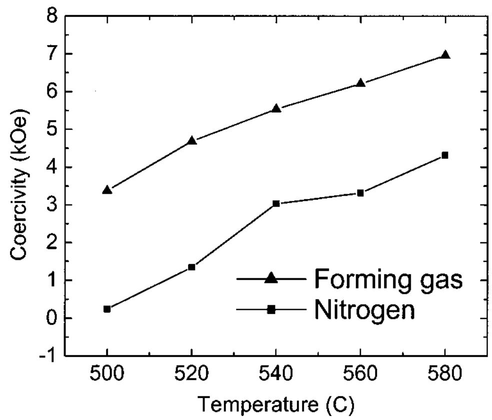


FIG. 1. Coercivity dependence on annealing temperature for samples annealed in nitrogen and forming gas, respectively, for 30 min.

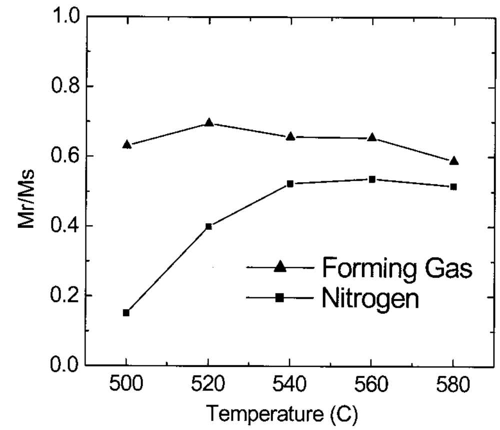


FIG. 2. Remanence ratio vs annealing temperature for samples annealed in nitrogen and forming gas, respectively, for 30 min.

and the decrease of interparticle distances resulting in particle aggregation as confirmed by *in situ* transmission electron microscopy studies. Previous experiments point out that the nanoparticles tend to aggregate when annealed at temperatures around 600 °C.[7] Above 600 °C, various degrees of aggregation of the particles result in exchange coupled assemblies.[8] It is expected that even higher annealing temperatures will eventually lead to significant agglomerations and formation of continuous films. In this article, we focus on annealing conditions below 600 °C.

Figure 1 shows the coercivity dependence on annealing temperature for the samples annealed in nitrogen and forming gas, respectively. It can be seen that the coercivity of the samples increases with increasing annealing temperature irrespective of the annealing atmosphere, due to the formation of the fct phase. However, the samples annealed in forming gas exhibit higher coercivity than those annealed in nitrogen at the same temperature. This may be attributed to the fact that annealing under forming gas reduces the surface iron oxide present in the assembly and facilitates the fct phase formation of the alloy.[9] The coercivity of the samples also changes with annealing time. For the samples annealed in nitrogen at 580 °C, the coercivity first increases as a function of annealing time, reaching a maximum of 5.25 kOe for 60 min annealing time, but drops drastically at longer annealing time. The increase in coercivity for 60 min annealing time is mainly due to the improvement in chemical ordering, though the possibility of sintering cannot be completely ruled out. However, annealing for too long a time results in grain aggregation and a decrease in coercivity of the nanoparticles, which may be related to the change in the magnetization reversal process from rotation type to nucleation type.[8] Another important parameter from the hysteresis loop of the FePt nanoparticles is the remanence ratio. The dependence of the remanence ratio on annealing temperature is shown in Fig. 2. The samples annealed in forming gas do not show much variation in the remanence ratios with varying annealing temperature. The samples annealed in nitrogen show increased remanence ratios with increasing annealing temperature. However, the remanence ratios for the samples annealed in nitrogen are lower than the remanence ratios for samples annealed in forming gas.

The $\delta M$ measurements were made for the samples annealed in forming gas to verify if there were any exchange interactions between the nanoparticles.[10] Before the measurements, the samples were treated in He atmosphere at 500 °C for 5 min to thermally demagnetize the samples and to randomize the orientations of the magnetic domains within the nanoparticles. The $\delta M$ curves for all the samples show a negative peak (see Fig. 3) indicating that the major interactions in the nanoparticles are dipolar-type and no exchange interactions exist between the nanoparticles.

The parameter for thermal stability ($KV/kT$) of the annealed FePt nanoparticle assemblies is derived from the time decay measurements. To measure the time decay, we first saturated the samples at the maximum field of 14 kOe for 3 s and then measured the remanent moment as a function of time for 1000 s at different reverse applied fields. The time dependent coercivity values obtained from these measurements were fitted using Sharrock's law,[11] and the thermal stability parameter $KV/kT$ was extracted from the fitting. The thermal stability parameter dependence on annealing temperature is plotted in Fig. 4. This figure shows resemblance to Fig. 1 in the sense that annealing under forming gas gives higher $KV/kT$ values than annealing in nitrogen

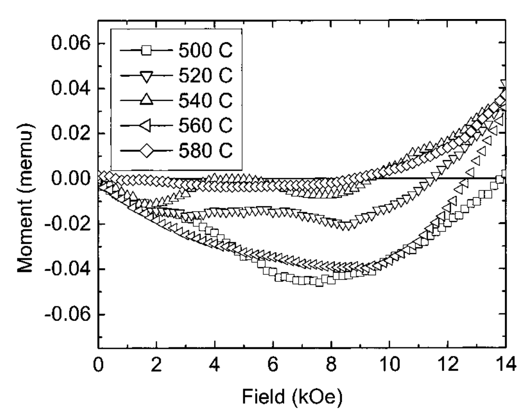


FIG. 3. The $\delta M$ curves for samples annealed in forming gas atmosphere for 30 min at varying annealing temperatures. The samples were demagnetized thermally by treating in He atmosphere at 500 °C for 5 min before making the $\delta M$ measurements.

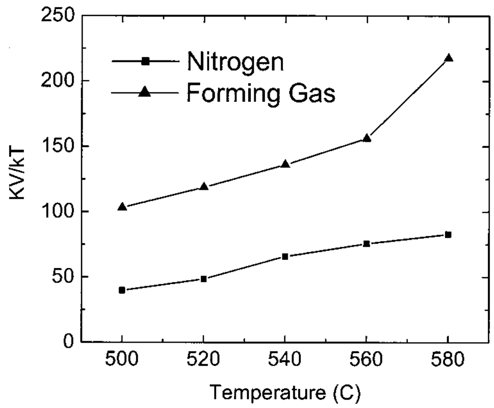


FIG. 4. KV/$kT$ dependence on annealing temperature for samples annealed in nitrogen and forming gas, respectively, for 30 min.

for the same annealing temperature. The maximum KV/$kT$ obtained was 218, for the sample annealed in forming gas at 580 °C for 30 min. This is much higher than the KV/$kT$ values for the current Co-based media at 40–60. Hence magnetic media based on patterned FePt nanoparticles annealed in forming gas would have good stability against thermal fluctuations.

The Curie temperature measurements for the samples annealed in nitrogen atmosphere for varying annealing times are shown in Fig. 5. Albeit a little noisy, the Curie temperatures can be well recognized from the graphs. The $M$-$T$ graph for the sample annealed for 10 min shows smaller slope during the paramagnetic transition than the samples annealed for longer times. This is due to the fact that annealing for longer time facilitates better chemical ordering of the fct phase. As expected, the Curie temperature increases with increasing annealing time and reaches 450 °C for the sample annealed for 120 min, which is close to the Curie temperature of bulk fct FePt phase.[12] From the sharp slope of the Curie temperature graphs of the samples annealed for 30, 60, and 120 min, we infer that the disordered–ordered transition takes place homogeneously in all the particles.

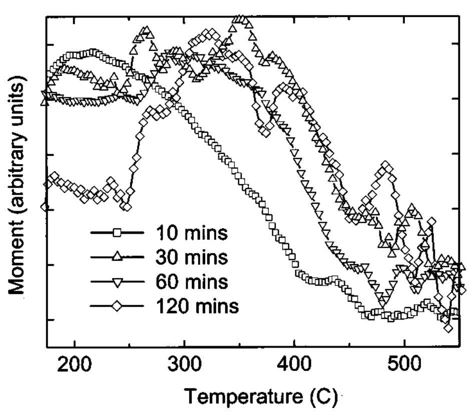


FIG. 5. Curie temperature graphs for the samples annealed in nitrogen at 580 °C for varying annealing time.

## IV. CONCLUSIONS

Systematic studies on the effects of annealing under nitrogen and forming gas atmospheres on the magnetic properties of the self-assembled FePt nanoparticles have been conducted with special attention to thermal stability characteristics. Postsynthesis annealing was found to enhance the magnetic properties of the nanoparticles. Annealing under forming gas produced higher coercivity and remanence ratio compared to annealing in nitrogen for the same annealing time and temperature. No significant aggregation or exchange interactions were observed in the samples annealed below 600 °C. The samples annealed in forming gas showed very high KV/$kT$ values. These self-assembled FePt nanoparticles are promising candidates for future ultrahigh density magnetic recording applications.

## ACKNOWLEDGMENTS

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