Silicide formation and particle size growth in high temperature annealed, self-assembled FePt nanoparticles

T.Thomson[1], M.F.Toney[2], S.Raoux[3], J.E.E. Baglin[3], S.L.Lee[4], S.Sun[5], B.D.Terris[1]

[1] Hitachi San Jose Research Center, 650 Harry Road, San Jose, CA 95120
[2] Stanford Synchrotron Radiation Laboratory, SLAC, Menlo Park, CA 94025
[3] IBM – Almaden Research Center, 650 Harry Road, San Jose, CA 95120
[4] School of Physics and Astronomy, University of St. Andrews, St. Andrews, Fife, UK
[5] IBM – T.J.Watson Research Center, Yorktown Heights, NY 10598

Abstract
High anisotropy, $L1_0$, FePt nanoparticle assemblies consisting of 4 nm diameter particles are considered a potential data storage medium beyond 1 Tbit/in^2. However, annealing at temperatures >500°C is required to form the high anisotropy phase. Recently work on the evolution of FePt nanoparticle assemblies as a function of annealing temperature has shown that for $T_{anneal} > 650$°C a substantial drop in magnetization is observed. Here we show that the observed reduction in magnetization is due to silicide formation as a result of a chemical reaction with the native oxide or Si substrate. We also show that the fraction of particles with $L1_0$ ordering increases as a function of annealing time with full $L1_0$ ordering established only after annealing at 725°C for 60mins. We note that particle agglomeration also occurs under these conditions.

INTRODUCTION

Monodisperse assemblies of high anisotropy, $L1_0$, FePt nanoparticles with diameters of the order of 4 nm are considered a potential data storage medium for densities beyond 1 Tbit/in^2 [1-3]. However, annealing at temperatures > 500°C is required to convert the as-deposited, chemically disordered face-centered cubic (fcc) FePt into the chemically ordered, high anisotropy $L1_0$ phase. This annealing step potentially allows a number of undesirable, thermally activated processes to occur including particle agglomeration and changes in oxidation state. We have recently reported [4-6] on the evolution of FePt nanoparticle assemblies as a function of annealing temperature. We noted that at annealing temperatures greater than 650°C a substantial drop in room temperature magnetization was observed, as measured from hysteresis loops using a maximum applied field of 9 Tesla. We have also previously reported [4, 6] that the fraction of FePt nanoparticles that are $L1_0$ ordered increases with annealing temperature. In this work we extend our study of both these effects through measurements on a series of nanoparticle assemblies annealed at a constant high temperature (725°C) for different times, using vibrating sample magnetometry (VSM), X-ray diffraction (XRD) and small angle neutron scattering (SANS). The progression of magnetic and structural properties with annealing time allows us to explain the reduction in magnetization and shows that full $L1_0$ ordering occurs only after extensive annealing. In addition coercivity and particle size data are consistent with a model where increasing particle size leads to a change in reversal mechanism.

EXPERIMENTAL

The nanoparticle assemblies were produced using a polymer mediated self assembly method [7-8]. The metal salt precursors for the nanoparticle synthesis were added in a ratio that produces $Fe_{58}Pt_{42}$ nanoparticles which have previously been shown to exhibit the highest coercivity (H_c) after annealing [1,8]. Alternate adsorption of a layer of polyethylenimine (PEI) and FePt nanoparticles onto a solid substrate resulted in nanoparticle assemblies with controllable thickness [7-8]. A total of 3 layers of PEI-FePt were deposited onto Si substrates with a native oxide surface layer. This technique provides thin assemblies consisting of particles with a diameter of ~4nm and a narrow size distribution (< 5%). The thin film PEI-FePt assemblies were annealed in a tube furnace with a flow of high purity helium gas at atmospheric pressure. During annealing the temperature was kept constant at 725°C while the time of annealing was varied between 2 and 120mins.

Magnetization data were collected using an Oxford Instruments VSM with a maximum applied field of 9 Tesla with a measurement temperature range from 1.65K to 350K. Non-linear background signals were measured and subtracted for each measurement temperature. In addition, linear background corrections from the substrate and PEI were determined from fits to the data at high applied fields. X-ray diffraction data were collected in a grazing incidence geometry at the National Synchrotron Light Source using beamline X20C. A grazing incidence geometry was used to minimize the background and the diffracted beam was analyzed with 1 milliradian Sollar slits. The data were analyzed to determine the Warren long-range order parameter S, which is unity for complete

chemical order, zero for chemical disorder, and proportional to the extent of chemical order for partial order [4,9].

SANS data were collected using instrument D11 at the Institut Laue Langevin in Grenoble, France using a neutron wavelength of $\lambda = 4.5\text{Å}$. Data were collected at three detector positions in order to scan a scattering vector, q, range of $0.012 - 0.3\text{Å}^{-1}$. Particle diameters were determined from the q dependence of the scattered intensity by matching the data to simulations of interacting, polydisperse hard spheres in the Percus-Yevick approximation using the method of Griffith et al. [10] modified to include a bimodal distribution [6].

RESULTS AND DISCUSSION

Figure 1 shows magnetization at 9 Tesla (M_{9T}) and H_c measured as a function of temperature between 20 and 350K for a series of PEI-FePt nanoparticle assemblies annealed for different times at a constant temperature of 725°C. The magnetization monotonically decreases with annealing time, while coercivity initially increases and then decreases after long anneal times. In the following two sections we propose a model consistent with XRD and SANS data that allows us to explain this magnetic behavior. In particular we focus on the decrease in M_{9T} and show how the choice of substrate can affect the properties of nanoparticle assemblies annealed at high temperature.

A. Magnetization

We first seek to explain the magnetization data. In addition to the reduction in M_{9T} with annealing time the data in fig.1(a) show that within the measurement temperature range there are no significant features in M_{9T} and that the functional form of the data is similar for all anneal times. Since the reduction in M_{9T} over this measurement temperature range is small, it is not possible to obtain an accurate value for the Curie temperature (T_c). However, a minimum bound can be set by comparing the data to the Curie-Weiss molecular field theory which gives $T_c > 600°C$. This is reasonable, as T_c for $L1_0$ ordered FePt is 750°C [11].

To explain the reduction in M_{9T} with annealing time we first consider the possibility of mass loss due to evaporation of material at high annealing temperatures. This potential source of M_{9T} reduction was eliminated by thermo-gravimetric analysis which showed that no significant mass loss occurred at the annealing temperatures employed here. The possibility of a chemical reaction with the native oxide surface or the Si substrate was investigated by XRD since both Fe and Pt can form silicides [12-13]. Fig.2 shows x-ray diffraction data which reveals the presence of diffraction peaks for both suessite (Fe_3Si) and xifengite (Fe_5Si_3) together with additional peaks. We have attempted to index these peaks, but have been unsuccessful; it is possible that these are from an silicide phase that is has not been observed previously. Although both Fe and Pt form silicides we did not observe any diffraction peaks associated with Pt silicides. These silicide x-ray peaks are not present in the short time (2min) annealed sample and neither have they been observed in similar, lower temperature annealed samples [6]. Hence we conclude that the appearance of Fe silicide is associated with high temperature annealing. Doping Si into Fe results in a reduced magnetic moment such that for a composition of $Fe_{0.5}Si_{0.5}$ the

moment is zero [14]. The value of the magnetization depends of the crystallographic phase and the local environment as is shown by the distribution of moment values given in [14]. Hence the formation of silicides provides an explanation for the reduction in M_{9T} per unit volume as the volume of FePt is reduced. The relative fraction of Fe silicide to FePt can be roughly estimated from the XRD data by assuming that the structure factors are the same for all the phases and that there is no preferred orientation [15]. This is shown in fig.3 together with room temperature M_{9T} data as a function of annealing time. The correlation between the M_{9T} and the relative fraction of $FeSi_x$ clearly implies that the reduction in M_{9T} is due to the formation of the $FeSi_x$ phases. An estimate of the average magnetization of the magnetic silicide phases can be made using the relative fraction x-ray data. This yields a value of $\sim 400 emu/cm^3$ which whilst a little lower than might be inferred from [14] is certainly reasonable. Since high temperature annealing is often necessary to complete the phase transformation from fcc to $L1_0$ in FePt nanoparticle assemblies, care needs to be exercised in an appropriate choice of substrate to ensure that chemical reaction does not occur with the substrate.

B. Coercivity

Fig.1(b) shows that the behavior of the nanoparticle array coercivity as a function of measurement temperature is more complex than that of the magnetization. Coercivity in thin nanoparticle assemblies is affected by at least three factors: (i) the conversion of FePt from the fcc to $L1_0$ phases, (ii) agglomeration of individual FePt nanoparticles to form larger entities and (iii) changes in reversal mechanism, for example, from coherent to incoherent rotation. Thus, in general, the physical origin of coercivity in these assemblies

is quite complicated with no single explanation offering a complete description. We have previously shown, through extensive x-ray studies [4], that our FePt nanoparticle assemblies consist of a mixture of fcc and $L1_0$ ordered regions (i.e., a two-phase system). Hence, we might expect coercivity to increase with the fraction of $L1_0$ ordered particles. Fig.4 shows the ordered fraction determined using XRD by the methods outlined in [9] together with H_c measured at T = 20K. Initially, both the ordered fraction and the H_c increase with annealing time. However, annealing for 60 and 120 min causes H_c to decreases significantly despite the fact that the $L1_0$ ordered fraction is close to one. The data, fig.1(b), also show that the measurement temperature dependence of H_c changes for the samples annealed for 60 and 120 mins such that there is less dependence of H_c on the measurement temperature.

We note that H_c(T=20K) is reduced for the 60 and 120min annealed assemblies compared with the 20min annealing condition. If we equate H_c(T=20K) with H_0, defined as coercivity in the absence of thermal effects (i.e. at T = 0K), then the anisotropy field (H_k), is given by $H_k=2H_0$ assuming a coherent rotation model. Hence, from these data we might suppose a reduction in H_k for longer anneals. However, since $L1_0$ ordering is fully developed, it seems unlikely that H_k is reduced significantly for the long anneals. SANS results shows that for the assemblies annealed for 2 and 20 mins the median particle sizes are 300Å and 550Å respectively, while the FWHM of the particle size distribution increases from 150Å to 180Å. These data, whilst subject to uncertainty due to the presence of silicides and q-range limitations, nevertheless show that both the median particle size and the width of the size distribution increases with anneal time. This is

consistent with data taken as a function of annealing temperature where a large increase in particle size and the size-distribution width were also found for nanoparticle assemblies annealed at >650°C [6]. The uncertainty introduced into the particle size analysis by the presence of silicides excludes further analysis for the 60 and 120min annealed assemblies. We speculate that if particle agglomeration continues for the 60 and 120min anneal samples then increased particle size could provide a means for a change in reversal mechanism leading to a change in the relationship between H_k and H_c.

CONCLUSIONS

We have studied the magnetic properties of FePt nanoparticle assemblies as a function of annealing time (2-120 mins) at constant temperature 725°C. Under these conditions FePt nanoparticle assemblies deposited onto native oxide Si substrates show a monotonic decrease in magnetization. We show that the decrease in magnetisation is due to a chemical reaction with the Si substrate leading to the formation of Fe silicides with a lower magnetization. The anneal temperature dependence of the coercivity is a result of a combination of changes in the relative fractions of fcc and $L1_0$ ordered FePt, particle agglomeration and possible changes in reversal mechanism.

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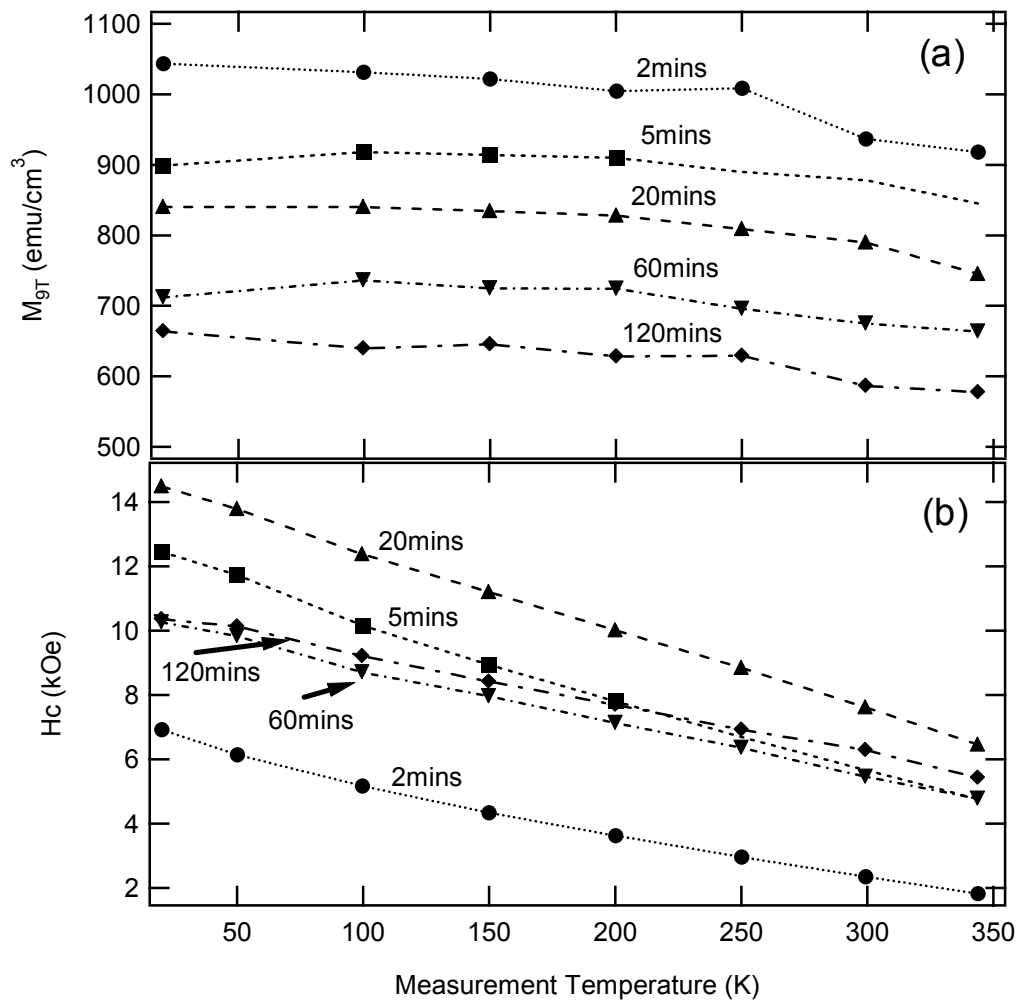[15] This is a rather crude approximation but since we have no data on the preferred orientation of the silicide phases it is not unreasonable.

Fig.1: Basic magnetic properties for FePt nanoparticle assemblies annealed for different times at a constant annealing temperature of 725°C, (a) magnetization at 9 Tesla and (b) coercivity as a function of measurement temperature. The dotted lines are included as a guide to the eye.
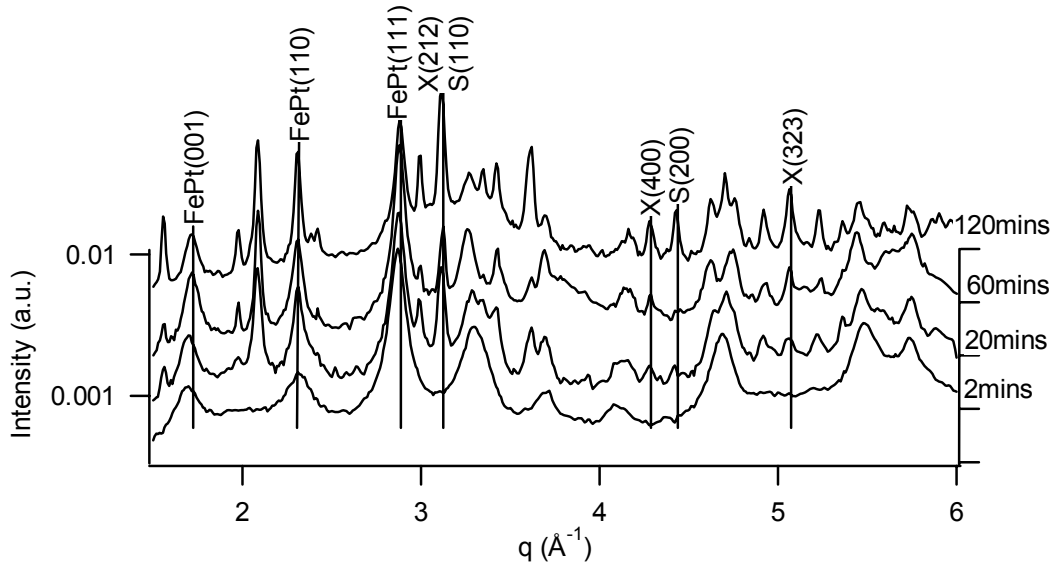
Fig.2: X-ray diffraction data showing the formation of Fe silicides as annealing time at 725°C increases. Selected FePt, suessite (Fe_3Si), marked as S, and xifengite (Fe_5Si_3), marked as X, peaks are identified.
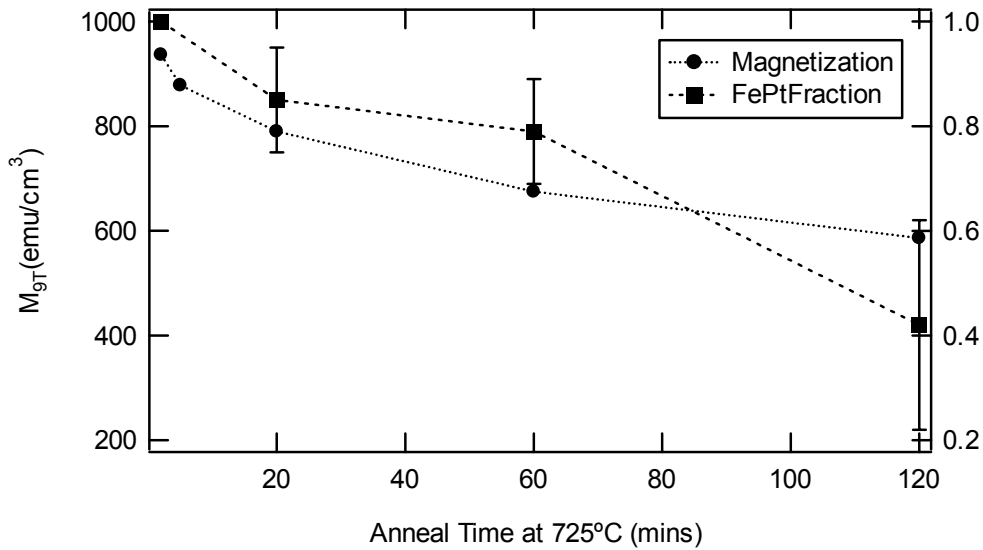

Fig.3: Magnetization measured at 9 Tesla and fraction of FePt as a function of annealing time at 725°C. The dotted lines are included as a guide to the eye.
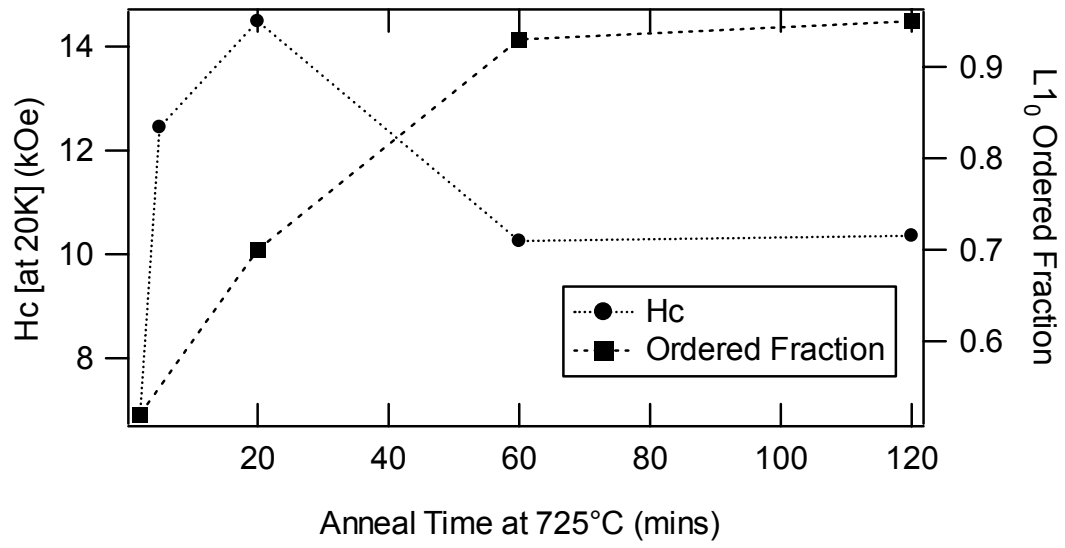
Fig.4: Coercivity measured at T = 20K and fraction of particles with $L1_0$ ordering as a function of anneal time. The dotted lines are included as a guide to the eye.