Lowering of the $L_{10}$ ordering temperature of FePt nanoparticles by He$^+$ ion irradiation

U. Wiedwald, a A. Klimmer, B. Kern, L. Han, H.-G. Boyen, and P. Ziemann
Institut für Festkörperphysik, Universität Ulm, Albert-Einstein-Strasse 11, 89069 Ulm, Germany

K. Fauth
Max-Planck-Institut für Metallforschung, Heisenbergstrasse 3, 70569 Stuttgart, Germany

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Arrays of FePt particles (diameter 7 nm) with mean interparticle distances of 60 nm are prepared by a micellar technique on Si substrates. The phase transition of these magnetic particles towards the chemically ordered $L_{10}$ phase is tracked for 350 kV He$^+$ ion irradiated samples and compared to a nonirradiated reference. Due to the large separation of the magnetically decoupled particles the array can be safely annealed without any agglomeration as usually observed for more densely packed colloidal FePt nanoparticles. The He$^+$ ion exposure yields a significant reduction of the ordering temperature by more than 100 K. © 2007 American Institute of Physics. [DOI: 10.1063/1.2472177]

Nanoparticles exhibiting a large magnetocrystalline anisotropy energy (MAE) density have attracted enormous attention over the last years due to their potential use in magnetic data storage. The equiatomic alloy system FePt with a MAE of up to $6 \times 10^5$ J/m$^3$ in its chemically ordered face-centered-tetragonal $L_{10}$ phase is appealing for this purpose since high MAE values can be established over a relatively wide composition range. Moreover, self-assembled FePt nanoparticles can be prepared by chemical methods in large amounts at low cost. It turns out, however, that the as-synthesized FePt particles exhibit the chemically disordered fcc phase with related low MAE values rather than the $L_{10}$ phase which is kinetically blocked. Consequently, annealing at temperatures above 600 °C is necessary to establish the technologically attractive, magnetically hard $L_{10}$ phase. FePt nanoparticles prepared by means of colloidal chemistry are typically only 2–4 nm apart after their self-assembled deposition on a support. The organic ligands cannot withstand high temperature annealing, which therefore gives rise to particle agglomeration. Removal of the ligand shell by O and/or H plasma exposure results in an improved anchoring of the particles to the substrate. Thus, the formation of larger particles can be remarkably reduced, but not totally avoided. It is therefore desirable to reduce the annealing temperature at which the structural phase transition to the $L_{10}$ phase occurs. Mainly two routes have been proposed: (i) the incorporation of a third element by a few at. %, which has the undesired side effect that for pseudobinary alloys the MAE is significantly decreased; (ii) the enhancement of the number of vacancies within the particles aiming at lowering the activation energy for diffusion. Previous ion irradiation experiments performed on FePt films and agglomerated particles suggest the application of He$^+$ bombardments to create defects while sputtering of atoms is almost completely suppressed. Thus, ion irradiation might also be a suitable method to reduce the transition temperature for well separated, individual nanoparticles which is in the focus of the current study.

The FePt nanoparticles are prepared by a micellar technique. Based on the self-organization of the diblock copolymer polystyrene-block-poly-2-vinylpyridine, micelles loaded with Fe and Pt metal-salts are deposited on substrates by dip coating. Exposure to an oxygen plasma nucleates the precursor to particles and removes the organics. By subsequent hydrogen plasma treatment, the particles can be reduced to their pure metallic state. Details on the preparation have been published elsewhere. For the micellar particles the interparticle spacing can be controlled over a much larger range (20–100 nm) than for FePt colloids opening the possibility to anneal the resulting array without forming agglomerates. Thus, the effect of He$^+$ ion irradiation on the ordering temperature of FePt nanoparticles can be determined on well separated, magnetically noninteracting particles for the first time.

FePt alloy particles with an average diameter of 7 nm are prepared on Si(001) substrates covered by native oxide. Irradiations were performed at a pressure of $1 \times 10^{-7}$ hPa and $T=300$ K with 350 keV He$^+$ ions at a fluence of $10^{16}$ He$^+$/cm$^2$. Simulation by SRIM delivers an average number of displacements per target atom of 0.08 together with a projected range of 1.5 μm for the present ions, i.e., practically all projectiles penetrate through the nanoparticles, produce defects there, and get stopped in the substrate. X-ray photoelectron spectroscopy (XPS) is used to track the particle cleanliness throughout the preparation. The composition of the studied particles is Fe$_{55}$Pt$_{45}$ as determined from XPS Fe-$2p_{3/2,1/2}$ and Pt-$4f_{7/2,5/2}$ line intensities with an estimated error of 3% assuming a homogeneous alloy. After irradiation, the samples are transported to beamline PM3 at Bessy II synchrotron facility (Berlin, Germany) in ambient conditions and, consequently, the particles are partially oxidized. Thus, a hydrogen plasma treatment (50 W rf power, 20 min, 300 °C) was applied to completely reduce the metal oxides prior to annealing. This process is performed in a custom-built chamber attached to the beamline endstation and characterized by means of x-ray absorption near-edge spectroscopy (XANES) and x-ray magnetic circular dichroism (XMCD) in the total electron yield mode. All measurements are performed at normal incidence of x rays collinear to the external magnetic field of ±3 T with a beam of 93% circular polarization. Magnetic hysteresis loops are taken at the maximum dichroic signal of the Fe-$L_3$ edge. The samples are...
successively annealed from 300 up to 770 °C in steps of about 100 K with a holding time of 30 min at each step. Before and after the complete annealing procedure, the particles are characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM) to determine particle diameters and to check for possible particle agglomerations. Figure 1 shows SEM images before the sample is exposed to \(10^{16} \text{He}^+/\text{cm}^2\) (a) and after annealing and magnetic characterization (b). The mean particle height is 7 nm with a full width at half maximum of 3 nm of a lognormal size distribution (inset of Fig. 1) as determined by AFM. High-resolution SEM and transmission electron microscopy (not shown) prove that the alloy particles have comparable lateral extensions, i.e., an approximately spherical shape. It is important to note that within the experimental error the size histograms are not changed, neither by annealing, in line with our previous observations, nor by the He\(^+\) bombardment.

Next, the magnetic properties of FePt particles will be discussed. For this purpose, in panels (a) and (b) of Fig. 2, XANES and XMCD spectra are presented, which were taken at \(T=11\ \text{K}\) on He\(^+\) bombarded FePt particles (a) and on a nonirradiated, but otherwise identically prepared sample (b). In both cases, the particles were treated in a hydrogen plasma at \(T=300 \ \text{°C}\) prior to spectroscopy. The absorption spectra reveal the pure metallic character of the FePt particles and XMCD shows the typical metallic Fe-\(L_{3,2}\) signature with total Fe magnetic moments of \(2.6 \mu_B - 2.8 \mu_B\) similar to recent results on corresponding colloidal nanoparticles but smaller than bulk samples. Panels (c) and (d) of Fig. 2 show the low temperature field dependence of the dichroic signal as related to (a) and (b). In this way, information on the hysteretic behavior of the particles is obtained and coercive fields of 600 and 1300 Oe are found prior to annealing for the irradiated particles and the reference, respectively. From simple Stoner-Wohlfarth model calculations we estimate an anisotropy energy density \(K\) of \((1 \pm 0.1) \times 10^5 \text{J/m}^3\) \([(2.3 \pm 0.3) \times 10^5 \text{J/m}^3]\) for the bombarded (reference) sample, which compares reasonably well to the fcc FePt bulk value of \(1 \times 10^5 \text{J/m}^3\). The effect of annealing on the hysteretic behavior of the FePt particles is demonstrated in panels (e) and (f), where the field dependence of the dichroic signal taken at 300 K is presented after annealing at \(T_A=770 \ \text{°C}\) for 30 min. As opposed to the nonannealed state, both samples exhibit now an open hysteresis loop at \(T=300\ \text{K}\), indicating the presence of \(L1_0\) particles. Most important, the He\(^+\) bombarded sample shows a room temperature coercive field \(H_C\) of 800 Oe as compared to 200 Oe of the nonbombarded reference. The remanent magnetization, however, is found significantly lower than \(0.5M_S\), which indicates that only a minority of particles has been fully transformed after this annealing step.

For a more quantitative analysis of the bombardment effect on the magnetic behavior of the particles after annealing, in Fig. 3 the evolution of coercive fields as a function of annealing temperature is presented for both low (11 K) and ambient temperatures (300 K). Starting from the small fcc phase values, increasing annealing temperatures result in a clear enhancement of \(H_C\) (11 K) in the case of the bombarded samples as opposed to the nonbombarded ones which show such a significant enhancement only after annealing at

FIG. 1. (Color online) SEM micrographs of 7 nm FePt nanoparticles prior (a) and after He\(^+\) ion irradiation and annealing up to \(T_A=770 \ \text{°C}\) (b). The mean separation of the particles is 60 nm. The size histogram of the particles is shown in the inset.
600 °C. Room temperature ferromagnetism arises at \(T_A\) close to 600 °C for the irradiated sample while annealing at 700 °C is necessary for the nonirradiated particles. In summary, the complete set of measurements of the ion irradiated sample is shifted by more than 100 K to lower annealing temperatures \(T_A\) as compared to the reference. For comparison, the coercive field of the reference sample after 270 min annealing at \(T_A=775\) °C is added to Fig. 3. This long time annealing has a similar effect on the particle ordering as short time annealing of the bombarded sample. One should note that the maximum available external field of ±3 T is not sufficient to saturate the particle ensemble once a huge MAE \((H_C > 5 \text{ kOe})\) is established. This leads to an underestimate of the corresponding \(H_C\) values above \(T_A=700\) °C.

The lower annealing temperatures necessary to form \(L1_0\) ordered particles can be discussed in terms of a reduced activation energy for diffusion \(E_D\) after He\(^+\) irradiation. The characteristic diffusion length \(\lambda\) depends on the diffusion coefficient \(D\) and the annealing time \(t_A\) via \(\lambda = \sqrt{Dt_A}\) with \(D = D_0 \exp(-E_D/(k_B T))\). Here, \(D_0\) is the pre-exponential factor, and \(k_B\) is Boltzmann’s constant.\(^{16}\) For alloys with a large uniaxial MAE, \(K\), it has been experimentally demonstrated that \(K\) has a nearly linear dependence on degree of chemical order \(S\).\(^{17,18}\) Thus, for Stoner-Wohlfarth particles with \(H_C \approx K/M\) \((M\) standing for their magnetization), the coercive field is directly proportional to the degree of chemical order \(S\) of a particle. As a result, it becomes possible to estimate the activation energy for diffusion \(E_D\) from hysteresis loops of noninteracting FePt particles assuming \((H_C-H_{CO})/H_{CO} \approx S/\lambda\), with \(H_{CO}\) denoting the initial coercive field. One should note that this assumption only holds well below full chemical order \(S \ll 1\). From Arrhenius plots of the quantity \(((H_C-H_{CO})/H_{CO})/t_A\) (not shown), activation energies of 0.7 eV for the He\(^+\) irradiated particles and 1.6 eV for the reference are derived. These energies are significantly smaller than the volume activation energy of 3.0 eV/atom reported for Pt in FePt.\(^{19}\) This may be related to the much stronger influence of surface diffusion in nanoparticles. Attributing the observed irradiation effect to defect enhanced diffusion rises the question as to why the bombarded particles exhibit a “defect memory” even though they are at least partly oxidized after the bombardment and subsequently reduced again prior to the magnetic measurements. The related defect behavior has still to be studied in more detail.

In summary, we demonstrate that irradiation of an array of 7 nm magnetically decoupled FePt nanoparticles with 350 keV He\(^+\) ions at a fluence of \(10^{16} \text{ ions/cm}^2\) results in a significant reduction of more than 100 K of the annealing temperature \(T_A\) necessary for their transformation into the \(L1_0\) phase. To arrive at this conclusion, XMCD hysteresis loops are determined as a function of annealing temperature and compared to a nonirradiated reference. Assuming a linear proportionality between the magnetic anisotropy and the degree of order, the \(T_A\) reduction after irradiation can be mapped onto a related decrease of the activation energy for diffusion \(E_D\) by more than 50%. The determination of activation energies by subsequent annealing will allow the direct comparison of hard magnetic nanoparticles prepared by different techniques in future studies.

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