Enhanced magnetic properties of FePt nanoparticles codeposited on Ag nanoislands

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Ag nanoislands have been used as nucleation sites for FePt nanoparticles when deposited on SiO₂ surfaces by electron beam evaporation. We demonstrate that it is possible to nucleate FePt nanoparticles on predeposited Ag clusters and that this results in a significant improvement of the hard magnetic Ag/FePt nanoparticles' properties. We find that, besides the usual annealing treatments, a simple predeposition of Ag nanoclusters promotes the formation of the FePt L1₀ phase at larger FePt nominal thicknesses (f_{FePt}). All the nanoparticles studied are ferromagnetic, except for those FePt samples deposited with lower nominal thicknesses ($f_{\text{FePt}} \sim 1.8$ nm), which are superparamagnetic. The presence of Ag seeds promotes the A1/L1₀ transition, which results in a remarkable enhancement of the coercivity (H_c) for both the as-deposited and the annealed samples. Maximum H_c of 8.9 and 9.4 kOe are obtained for the Ag/FePt nanoparticles with $f_{\text{FePt}} \sim 1.8$ and 3.5 nm, respectively. Our results are a strong indication that the nucleation of the FePt nanoparticles on Ag nanoclusters can promote significant magnetic hardening of the FePt nanoparticles by easing the transition from the disordered to the ordered phase. © 2009 American Institute of Physics. [DOI: 10.1063/1.3116558]

I. INTRODUCTION

In recent years, significant scientific and technological effort has been devoted to research on FePt nanoparticles for high density recording media,¹ high performance nanocomposite magnets,¹ and multifunctional systems for integrated circuitry.^{2,3} The community's interest in this material lies in the magnitude of the anisotropy constant of the L1₀ ordered phase,¹ which enables us to prevent the formation of the superparamagnetic state at room temperature for particles as small as 3 nm (in diameter).^{4,5}

The L1₀ ordered phase of the FePt bulk alloy is thermodynamically more stable¹ than the A1 disordered phase, up to a critical temperature $T_c \sim 1300$ °C. The growth of FePt nanostructures at relatively low substrate temperature (T_s) results in the formation of the metastable A1 structure.^{6,7} Thus, to obtain FePt nanoislands of the L1₀ phase, it is necessary to use high T_s (Ref. 6) or thermal annealing.^{7,8} More recently, introducing immiscible metallic additives, such as Au, Cu, and Ag,^{9–14} has been shown to promote the ordering transformation at lower T_s , by providing a decrease in the activation energy.¹⁰ Until now, this concept has been demonstrated only on nanoparticles^{9,11,12,14} synthesized with chemical methods on thin films¹⁰ and on multilayer structures.¹⁴ While thin film deposition methods are ubiquitous in a wide range of nanomaterial technologies, mainly because of their simplicity and flexibility, but also because of their high yields in industrial processes, there is no evidence in the literature of free standing Ag/FePt nanoparticles prepared using such techniques. This is due to the fact that the formation

of nanoparticles by deposition methods is possible only within a narrow range of growth parameters.¹⁵ However, although the deposition of metals in a subpercolation regime is a complex process, in principle, Ag nanoclusters grown before the deposition of FePt could act as nucleation sites for the subsequent deposition of FePt nanoparticles.

The aim of the present study is to investigate the effect of Ag nanoclusters (predeposited on SiO₂/Si substrates by e-gun evaporation) on the structural, morphological, and magnetic properties of Ag/FePt nanoparticles formed during a second step of Fe and Pt codeposition. This study compares Ag/FePt with FePt nanoparticles, where the Ag deposition step has been omitted and codeposited on Si/SiO₂ wafers under identical conditions.

II. EXPERIMENTAL

Ag, FePt, and Ag/FePt nanoparticles were deposited by electron beam coevaporation at a base pressure of 2×10^{-7} mbar with a substrate temperature (T_s) of ~ 500 °C.¹⁵ All specimens were grown on thermally oxidized silicon (100) substrates with a SiO₂ amorphous layer of ~ 100 nm on top. The FePt were prepared by codeposition of Fe and Pt, while the Ag/FePt nanoparticles were prepared in two steps: the initial deposition of Ag particles and the subsequent codeposition of Fe and Pt, under identical conditions. In all depositions the partial deposition rate was ~ 0.030 nm/s when depositing Fe and 0.033 nm/s when depositing Ag or Pt. The Fe and Pt deposition rates led to an approximate atomic ratio Fe:Pt ~ 1 . The deposition rate for each material was controlled by an independent quartz crystal thickness monitor.

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TABLE I. Main growth parameters (f is the total thickness and f_{FePt} is the FePt nominal thickness) and the most relevant morphological (D_p is the mean particle size and δ is the particle density) and magnetic (H_c is the perpendicular coercivity) properties of the FePt and Ag/FePt nanoparticles.

	ID sample	f (nm)	f_{FePt} (nm)	D_p (nm)	δ ($\times 10^{11}/\text{cm}^2$)	H_c (kOe)
Ag	...	1.5	...	7.0	5	...
FePt	A	3.5	3.5	6.9	8.8	1.9
	B ^a	3.5	3.5	8.1	8.3	7.7
	C	1.8	1.8	5.4	18.8	0
	D ^a	1.8	1.8	5.4	13.1	0.1
Ag/FePt	E	5	3.5	9.1	5.8	2.6
	F ^a	5	3.5	8.4	3.6	9.4
	G	3.3	1.8	5.5	12.2	3.1
	H ^a	3.3	1.8	5.6	7.4	8.9

^aSamples annealed at 700 °C *in situ* 5 min. immediately after deposition.

In Table I, we define samples A–H according to their deposition and annealing conditions and show the nominal thickness of the layer f , the mean crystallite size D_{cryst} , the mean particle diameter D_p , the particle density δ , and the coercivity H_c measured along the perpendicular direction with respect to the substrate plane. Selected samples were annealed at 700 °C for 5 min in vacuum, immediately after their deposition.

The structural and morphological properties of the samples were analyzed by x-ray diffraction (XRD) and transmission electron microscopy (TEM). The x-ray diffractometry was performed with Cu $K\alpha$ radiation; the mean crystallite size D_{cryst} was estimated by line broadening analysis on nonoverlapping peaks, using the Scherrer formula. TEM was performed with a Philips CM20. This instrument has high resolution capabilities and is equipped with an energy dispersion x-ray spectrometer for quantitative chemical characterization and a Gatan Imaging Filter for the acquisition of electron energy loss spectra and energy filtered TEM (EFTEM) images. The magnetic properties of the FePt nanoislands were measured using a magneto-optical Kerr effect magnetometer at room temperature (a maximum field of 22 kOe). Corrections for self-demagnetization, to determine the exact internal field of the samples during the magnetic measurements, were not performed.

III. RESULTS AND DISCUSSION

The crystallographic characterization of the Ag/FePt nanoparticles described in this study deals with two challenges: (i) the so-called “nanostructure problem,”¹⁶ i.e., the difficulty to characterize the crystallographic structure of material within the 1–10 nm scale, and (ii) the small quantity of material detectable by XRD, TEM, or other techniques. For this reason, since the nominal thickness of the FePt nanoparticles described in this study is within the 1.8–3.5 nm range, TEM or XRD techniques cannot provide a complete and conclusive information on their crystallographic structure. For this reason, it is necessary to combine complementary methods, i.e., XRD, TEM, and magnetometry, to infer the collective crystallographic structure of the FePt and Ag/FePt nanoislands.

A. Morphological properties

It is well known that during the first deposition stage of metals on amorphous oxides, isolated islands form according to the Wolmer–Weber growth mechanism.¹⁷ During the initial stage of the coarsening process, there are small and large nanoislands and the particle size distribution (PSD) is bimodal. The equilibrium density of the nanoparticles (δ_{eq}) is achieved as a consequence of the higher bidimensional evaporation rate of the smaller clusters than the larger ones¹⁸ (Ostwald ripening). Consequently, at equilibrium, the smallest clusters disappear and the PSD becomes monomodal. The radius of curvature (R) and δ_{eq} of metallic nanoparticles, grown according to the Wolmer–Weber mechanism, depends on the temperature T_s and the surface energy of the nanoparticles (γ_n). Their relationship is described by the Gibbs–Thomson equation:¹⁸

$$\delta_{\text{eq}} = \delta_{\infty} \exp\left(\frac{\gamma_n}{\rho K_B T_s R}\right), \quad (1)$$

where δ_{∞} is the density of particles of infinite size, ρ is the density of the material ($\rho \sim 10.5$ and 15.0 g/cm³ for Ag and FePt, respectively¹⁹), K_B is the Boltzmann constant, and γ_n is the surface energy of a nanoparticle [1.2 and 17.2 J/m² for Ag (Ref. 20) and FePt,¹⁵ respectively]. As a consequence, the island density δ and the curvature R of different materials, deposited under the same growth conditions, depend on the γ_n/ρ ratio. Ag and FePt exhibit γ_n/ρ ratios of 0.11 and 1.15, respectively. Consequently, the growth of the FePt alloy nanoparticles would lead to a larger δ when compared to the nanoisland density of the silver nanoparticles, with the same nominal thickness f . The growth of Ag at 500 °C with a nominal thickness of 1.5 nm on SiO₂ results in the formation of droplike nanoparticles, as can be seen in the in-plane TEM images shown in Fig. 1(a), with a monomodal PSD and a mean particle size $D_p \sim 7$ nm [see Fig. 1(b) and Table I]. Figure 2 shows a comparison of in-plane TEM images of nanoparticles grown without Ag [Figs. 2(a)–2(d), FePt] and after the deposition of the silver clusters [Figs. 2(e)–2(h), Ag/FePt]. All the as-deposited FePt samples [Figs. 2(a) and 2(c)] consist of elongated particles, suggesting that a droplet/coalescence transition^{21,22} has occurred, while their PSDs’ are bimodal and monomodal [empty squares in Figs. 3(a)

FIG. 1. (a) In-plane bright field TEM image and (b) PSD of the Ag nanoparticles.

and 3(b), respectively]. Interestingly, although the nominal thickness of C samples (FePt) is just 1.2 times higher than in our pure Ag particles, their nanoisland density is more than three times larger (Table I). As mentioned above, this is consistent with the higher γ_n/ρ ratio of FePt than Ag particles, which leads to larger δ .

The postdeposition annealing at 700 °C for 5 min led to a decrease in the island density [Figs. 2(b) and 2(d), Table I] and an increase in the interparticle distance for both specimens (B and D samples) as a consequence of the thickening of the nanoparticles¹⁷ and the Ostwald ripening.¹⁸ Despite the thermal annealing, the PSD of B samples is bimodal [full squares in Fig. 3(a)] suggesting, as mentioned above, that the nanoparticles are not in their equilibrium distribution. Conversely, the postannealing effect on the PSD of the FePt with $f \sim 1.8$ nm [full squares in Fig. 3(a)] results in a sharpening of the monomodal PSD. Although the thermal annealing usually leads to an increase in the mean nanoisland size, as occurred for the nanoparticles with $f \sim 3.5$ nm, this trend can be counterbalanced by the thickening of the islands¹⁷ as observed in the D samples.

The predeposition of Ag seeds results in an increase in D_p and a decrease in δ in the Ag/FePt samples with $f_{\text{FePt}} \sim 3.5$ and 1.8 nm, as can be seen in Table I and Figs. 2(e)–2(h). This is due to the larger total thickness, $f \sim 5.0$ and 3.3 nm, respectively. The PSD of the Ag/FePt nanoparticles is broader than the FePt samples.

B. Structural properties

The XRD patterns obtained for the Ag nanoparticles (not shown here) exhibit no evidence of Ag peaks due to the low diffracting volume of the deposited material. Figure 4 shows the XRD patterns of the as-deposited and annealed FePt and Ag/FePt samples, with $f_{\text{FePt}} \sim 3.5$ nm (A, B, E, and F samples). The diffraction peaks are very broad due to the small crystallite size (different from D_p). According to previous studies,¹⁵ the position of the diffraction peak of FePt nanoparticles has to be attributed to their crystallographic structure rather than other effects such as stress. Comparing the observed peak position with the (111) A1 and $L1_0$ diffraction lines, it is clear that the as-deposited FePt nanoparticles (A samples) have the A1 structure mainly, while their annealing shifts the peak toward the (111) $L1_0$ line (B samples). The (111) peak of the as-deposited Ag/FePt nanoparticles (E samples) encompasses both the A1 and the $L1_0$ lines indicating the presence of both phases. Their subsequent annealing (F samples) leads to a shift of the diffraction peak toward the $L1_0$ line, i.e., a significant volume fraction of the nanoparticles undergoes the A1/ $L1_0$ transition.

Figure 5 shows the XRD patterns of the as-deposited and annealed FePt and Ag/FePt samples, with $f_{\text{FePt}} \sim 1.8$ nm (C, D, G, and H samples). Both the as-deposited and annealed FePt nanoparticles (C and D samples) exhibit a large volume fraction of A1 phase, inferred from the experimental peak position's coincidence with the A1 (111) diffraction line. It is not clear to what extent the as-deposited Ag/FePt nanoparticles (G samples) exhibit the $L1_0$ ordered structure, while the annealed Ag/FePt nanoparticles (H samples) do show the $L1_0$ structure. These results are a strong indication that the addition of Ag favors the A1/ $L1_0$ phase transition. Since there is no evidence of Ag diffraction peaks even for pure Ag nanoparticles, it is not clear if the order/disorder transition in the FePt nanoparticles is due to the metastable incorporation of Ag in the FePt,^{7,14} which favors the kinetic ordering of the Fe and Pt during the Ag segregation and vacancy formation or to the local strain resulting from the Ag segregated at the boundary of the FePt nanoparticles.⁸ In order to elucidate

FIG. 2. In-plane bright field TEM image for (a) A samples, (b) B samples, (c) C samples, (d) D samples, (e) E samples, (f) F samples, (g) G samples, and (h) H samples.

FIG. 3. PSDs for (a) A and B, (b) C and D, (c) E and F, and (d) G and H samples. The empty and full squares represent the as-deposited and annealed samples, respectively.

this, compositional maps were obtained by EFTEM analysis on selected specimens. For this purpose, we used the Fe $L_{3,2}$ and Ag $L_{3,2}$ electron energy loss spectroscopy peaks in order to apply the three window method²³ for the acquisition of the Fe and Ag EFTEM images, respectively. As can be seen in Fig. 6, the in-plane bright field TEM image of F samples [Fig. 6(b)] overlaps to a great extent with the Ag and Fe maps [Figs. 6(a)–6(c)], something which becomes more visible in larger particles. This is a strong indication that (at least for the larger particles) is possible to grow FePt on Ag nanoclusters and form Ag/FePt free standing nanoparticles using a simple thin film deposition technique.

It is well known that the self-diffusion activation energy of atoms in metals or alloys is related to the strength of their bonding^{24,25} and, thus, to their surface energy.²⁶ Therefore, the reduction in surface energy promoted by the presence of

FIG. 4. XRD patterns of the FePt (A and B samples) and Ag/FePt (E and F samples) nanoparticles with $f_{\text{FePt}} = 3.5$ nm.

FIG. 5. XRD patterns of the FePt (C and D samples) and Ag/FePt (C and H samples) nanoparticles with $f_{\text{FePt}} = 1.8$ nm.

a surfactant in nanoparticles, such as Ag on FePt, can lead to higher mobility of the atoms and thus explain the increase in their kinetic ordering. This diffusion enhancement is also consistent with the increased grain growth¹² and the kinetics of the A1/L1₀ transition,¹⁰ observed in FePt nanoparticles, promoted by the addition of Ag in our samples.

C. Magnetic properties

Figure 7 shows the magnetization curves, measured along the perpendicular direction with respect to the plane of the substrate, of the FePt (A–D samples) and the Ag/FePt (E–H samples) nanoparticles. The FePt specimens with $f_{\text{FePt}} \sim 3.5$ nm are ferromagnetic [Figs. 7(a) and 7(b)], with a coercivity H_c that increases from 1.9 to 7.8 kOe after thermal annealing, as a consequence of the postannealing structural ordering discussed above. Conversely, the as-deposited FePt nanoparticles with $f_{\text{FePt}} \sim 1.8$ nm (C samples) are superparamagnetic [Fig. 7(c)], confirmed by the fit of the experimental data with the Langevin curve. This is consistent with their disordered crystallographic structure (Fig. 4) and with the fact that their D_p is smaller than the superparamagnetic critical size (~ 9 nm for A1 FePt nanoparticles). After annealing, the nanoparticles become ferromagnetic [Fig. 7(d)]. Although the XRD patterns of the specimens with $f_{\text{FePt}} \sim 1.8$ nm show no significant structural transition in the L1₀ ordered phase after annealing (Fig. 5), the hour-glass shape of the magnetization curve of the annealed nanoparticles (D samples) suggests the coexistence of nanoislands with the A1

FIG. 6. (a) In-plane bright field TEM image and the EFTEM elemental maps from the same area indicating the presence for Ag (b) and Fe (c).

FIG. 7. Magnetization curves measured along the perpendicular direction with respect to the plane of the substrate for (a) A samples, (b) B samples, (c) C samples, (d) D samples, (e) E samples, (f) F samples, (g) G samples, and (h) H samples.

and $L1_0$ crystallographic structures. Figures 7(e)–7(h) show the magnetization curves for the Ag/FePt nanoparticles. As can be seen, the use of Ag seeds results in a significant ferromagnetic hardening of the samples, with the maximum $H_c=9.4$ kOe obtained for the annealed nanoparticles with $f_{\text{FePt}} \sim 3.5$ nm (F samples). Another remarkable result concerns the Ag/FePt nanoparticles with $f_{\text{FePt}} \sim 1.8$ nm [Figs. 7(g) and 7(h)]. While the as-deposited and the annealed FePt particles are superparamagnetic and ferromagnetically soft, respectively, [Figs. 7(c) and 7(d)], a simple predeposition of Ag clusters results in the significant magnetic hardening of the final nanoislands. These results show that the Ag seeds can be used to favor the $A1/L1_0$ transition successfully, promoting a significant magnetic hardening of the deposited FePt nanoparticles.

IV. CONCLUSIONS

The present study demonstrates that it is possible to nucleate FePt nanoparticles on Ag clusters using thin film deposition techniques and discusses the structural, morphological, and magnetic properties of FePt and Ag/FePt nanoparticles deposited on SiO_2 . The mean particle size increases with an increase in the total nominal thickness of the samples and the addition of Ag leads to a broadening of the PSD. The formation of the $L1_0$ phase is favored at larger f_{FePt} , by the annealing treatment and by the use of Ag nanoclusters as nucleation sites for the FePt nanoparticles. All nanoparticles are ferromagnetic, except the FePt samples deposited with $f_{\text{FePt}} \sim 1.8$ nm, which are superparamagnetic. The presence of Ag seeds results in a remarkable coercivity enhancement both for the as-deposited and annealed samples with maximum H_c of 8.9 and 9.4 kOe obtained for the Ag/FePt nanoparticles with $f_{\text{FePt}} \sim 1.8$ and 3.5 nm, respectively. Our results indicate that it is possible to favor the disorder/order transition and promote a significant ferromagnetic hardening of FePt nanoparticles by using Ag nanoclusters, grown by thin film deposition techniques, as nucleation sites.

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