Synthesis, chemical ordering, and magnetic properties of self-assembled FePt–Ag nanoparticles

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$[FePt]_{1-x}Ag_x$ nanoparticles were chemically synthesized. Self-assembled arrays were characterized by transmission electron microscopy and small angle x-ray diffraction (XRD). Particles were annealed at temperatures from 300 to 500 °C for 30 min and degree of chemical ordering was characterized by large angle XRD and by magnetometry. Compared with pure FePt nanoparticles, additive Ag reduced the A1 to $L1_0$ ordering temperature by more than 100 °C. A maximum coercivity of more than 10 kOe was measured for samples with ~15% Ag annealed at 500 °C, compared with about 2 kOe for samples without Ag. This reduction in required annealing temperature significantly reduces particle coalescence and loss in positional order. XRD measurements suggest that the reduction of the ordering temperature is due to defects and lattice strain introduced by the Ag and the subsequent segregation of the Ag upon annealing, activating the nucleation of the ordered phase. © *2003 American Institute of Physics.*
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The FePt alloys have been investigated for several decades because of their important applications in permanent magnetics and ultrahigh-density magnetic recording media.[1–13] It was recently demonstrated that uniformly size spherical FePt nanoparticles can be synthesized that will self assemble into highly ordered three-dimensional superlattices films. The films were thermally annealed to produce the high anisotropy $L1_0$ phase while maintaining particle order.[5,14] However, annealing above 550 °C is necessary to obtain a high degree of ordering of pure FePt nanoparticles.[5,14–19] From a practical viewpoint, such high temperature processing is unsuitable for mass-production of magnetic recording media. In addition, sintering of FePt nanoparticles occurs at high annealing temperatures. Recently Kitakami *et al.* found that the addition of Sn, Pb, Sb, Bi, and Ag into sputtered CoPt thin films promotes a disordered–ordered transformation, resulting in an appreciable reduction of the temperature for ordering.[20,21] They also stated that the ordering is promoted by defects produced by the additives during annealing, because those additives have very low surface energy and are easy to segregate.[22] For self-assembled FePt nanoparticles which have potential applications for future high density recording media, there is no known published work on lowering the ordering temperature. The present article gives an account of the synthesis and phase transition of self-assembled FePt-Ag nanoparticles.

As a first attempt, a series of $[FePt]_{1-x}Ag_x$ nanoparticles was chemically synthesized. Unlike the sputtered thin films using a Ag target, a suitable chemical procedure must be found to synthesize FePt–Ag nanoparticles. We used a method similar to that reported by the IBM group for FePt nanoparticles and added silver acetate to the reaction.[5,14] The synthesis of the FePtAg nanoparticles was obtained by the thermal decomposition of iron pentacarbonyl and the reduction of platinum acetylacetonate and silver acetate with 1,2-hexadecanediol in phenyl ether. Oleic acid and oleylamine were added to provide a surfactant layer for the nanoparticles. The FePt–Ag particles were precipitated and rewashed with ethanol and separated by centrifugation. The particle precipitant was purified by redispersing in hexane and reprecipitating by adding ethanol. The particles were then dispersed in a mixture of hexane and octane that included small amounts of oleic acid and oleylamine. The dispersion were dropped onto carbon-coated copper transmission electron microscopy (TEM) grids and silicon wafers, and the solvent evaporated to give self-assembled films.

X-ray diffraction (XRD) experiments were performed in the reflection geometry with a Philips X'Pert Materials Research Diffractometer (X'Pert-MRD) and a Rigaku powder diffractometer, both using Cu $K\alpha$ radiation. The modulated structure of the self-assembled multilayers was confirmed from the existence of several superlattice peaks at low scattering angle [Fig. 1(a)]. Furthermore, the position of the high-angle peaks showed that as-made nanoparticles exhibit a chemical disordered fcc structure with three-dimensional (3D) random orientation. Compared with pure as-made FePt nanoparticles, the (111) peak of FePt–Ag nanoparticles was shifted to the low angle, which means the lattice of FePt nanoparticles was expanded after the addition of Ag.

Heat treatments were done in a Lindberg tube furnace in an Ar atmosphere with 2% hydrogen at a temperature of 300–500 °C for 30 min. Figure 2 illustrates the development of the chemically ordered $L1_0$ phase of FePt nanoparticles with the addition of 15% Ag. During annealing, the Fe and Pt atoms start to rearrange into the long-range chemically ordered fct structure, as indicated by the (111) peak shifts, the evolution of the (001) and (110) peaks, and the splitting of (200) and (002) peaks. In Fig. 2, very weak superstructure (001) and (110) peaks from the ordered $L1_0$–FePt appear at

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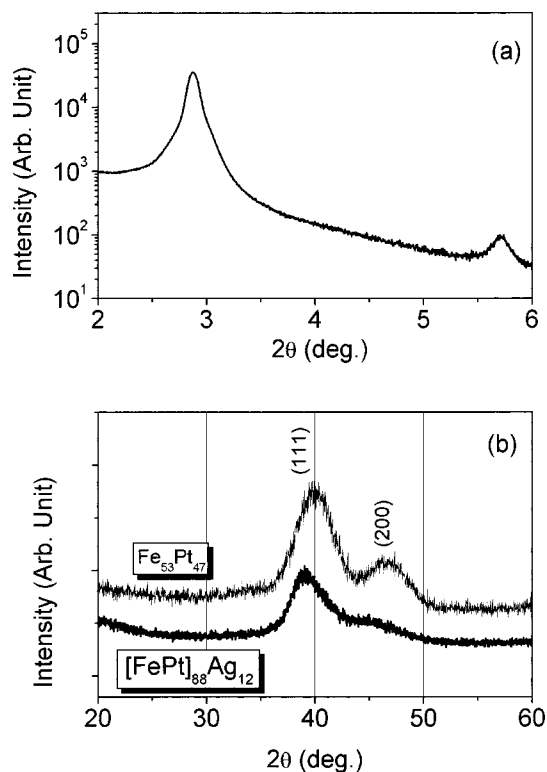
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FIG. 1. (a) Small angle XRD profile of as-made $[FePt]_{88}Ag_{12}$ nanoparticles. (b) Large angle XRD profile of as-made 3.5 nm $[FePt]_{88}Ag_{12}$ and 4 nm $Fe_{53}Pt_{47}$ nanoparticles. (All particle compositions were determined by energy-dispersive x-ray analysis.)

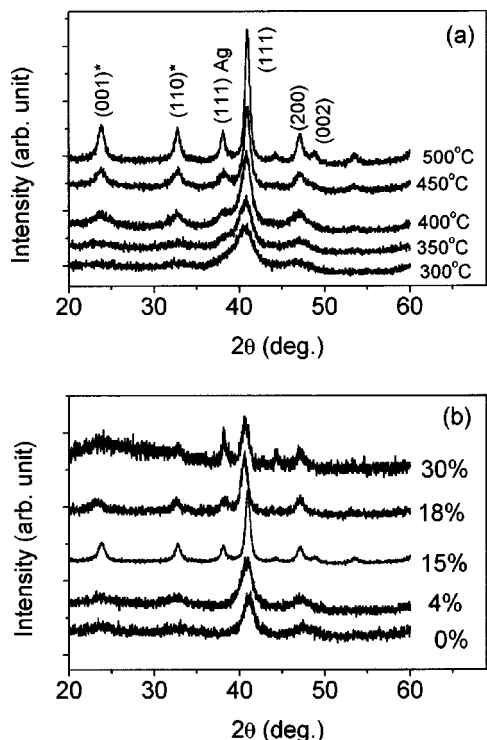an annealing temperature, T_{ann}, of $\sim 300\,°C$, indicating that partial ordering begins around this temperature. This temperature, however, was reduced by $\sim 100-150\,°C$ compared with that of self-assembled FePt nanoparticles with no additive.[5,14] It is worth mentioning, however, that the exact structure after thermal annealing depends on annealing temperature, as well as concentration of Ag. Figure 2(b) shows a series of XRD patterns of FePt nanoparticles with different concentration of Ag. It shows that among these particular compositions, samples with $\sim 15\%$ Ag additive yield the best chemical ordering when annealed at 500 °C.

Figure 3(a) shows a TEM image of a film of FePt nanoparticles with 12% Ag before annealing. The image shows an array of well-separated, uniformly sized particles of diameter 3.5 nm that form a hexagonal 3D superlattice. After annealing at 400 °C [Fig. 3(b)], the nanoparticles retain their superlattice structure, except that a few particles show slight aggregation.

Magnetic measurements were made using a Princeton Measurements Model 2900 alternating gradient magnetometer. Figure 4 shows the in-plane hysteresis loops of self-
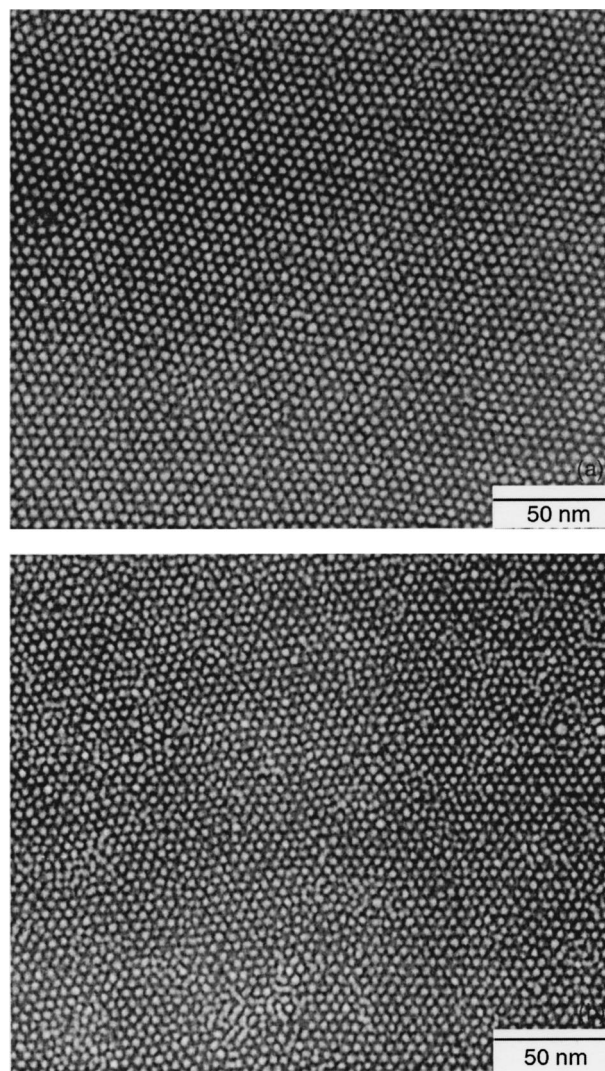

FIG. 2. (a) XRD profile of self assembled $[FePt]_{88}Ag_{12}$ nanoparticles annealed at different temperatures. (b) XRD patterns of $[FePt]_{1-x}Ag_x$ nanoparticle assemblies annealed at 500 °C for 30 min ($x = 0\%, 4\%, 15\%, 18\%, 30\%$).

FIG. 3. TEM images of self-assembled $[FePt]_{88}Ag_{12}$ nanoparticles for films (a) as made and (b) annealed at 400 °C for 30 min.

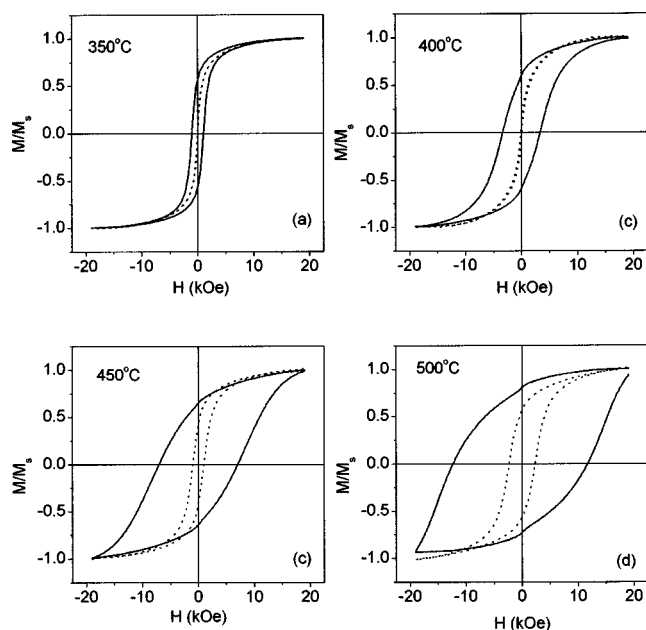FIG. 4. In-plane hysteresis loops of self-assembled $[FePt]_{88}Ag_{12}$ (solid line) and $Fe_{53}Pt_{47}$ (dot line) nanoparticle arrays annealed at different temperatures for 30 min.

FIG. 5. Coercivity vs concentration of Ag for self assembled $[FePt]_{1-x}Ag_x$ nanoparticles annealed at 500 °C for 30 min. The solid line indicates the coercivity of $Fe_{53}Pt_{47}$ nanoparticles annealed at the same condition. The dotted line is drawn as a guide to the eye.

assembled FePt nanoparticles with 15% Ag annealed at different temperatures for 30 min. For comparison, the loops of pure self assembled $Fe_{53}Pt_{47}$ nanoparticles annealed under the same conditions are also plotted. It is clear that the addition of Ag significantly enhances the effect of annealing on the coercivity. For the FePt–Ag nanoparticles, a coercivity of more than 10 kOe was measured after annealing at 500 °C; however, the actual coercivity probably exceeds this value since the maximum field of 19 kOe is not enough to fully saturate the loop. Without the addition of Ag, H_c is only about 2 kOe after annealing at 500 °C. Figure 5 shows the dependence of in-plane coercivity H_c on concentration of Ag for self-assembled $[FePt]_{1-x}Ag_x$ nanoparticles. It is obvious that the coercivity was significantly enhanced with ~15% Ag. These results clearly show that the Ag additive significantly lowers the annealing temperature necessary for high H_c.

As mentioned above, the lattice of FePt nanoparticles with Ag additive was expanded because the atomic volume of Ag (10.3 cm^3/mol) is larger than that of Fe (7.1 cm^3/mol) and Pt (9.1 cm^3/mol).[23] Thus, the elastic energy of the FePt system increased. On the other hand, the Ag has a low surface energy and is easy to segregate.[22] It appears that the Ag atoms leave the FePt lattice at low temperature, leaving lattice vacancies. These vacancies together with increased elastic energy of the FePt system increase the mobility of the FePt atoms to rearrangement, and as a result, the kinetics of the ordering process is enhanced.

In summary, we have synthesis self assembled FePt–Ag nanoparticles and found that the annealing temperature for ordering of $L1_0$–FePt nanoparticles can be lowered to ~400 °C at 30 min by addition of Ag. This remarkable reduction of the annealing temperature is probably related to the defects and lattice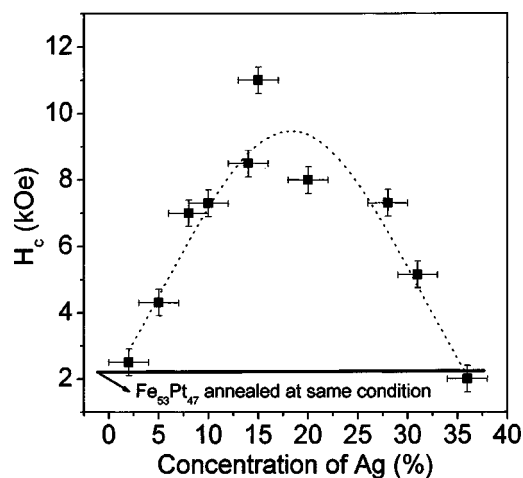 strain introduced by the Ag and the segregation of the Ag upon annealing. An important question is what happen to the Ag during the ordering process. This will be addressed in future investigations.

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