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Compositional stability of FePt nanoparticles on SiO_2/Si during annealing

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The loss of Fe due to oxidation or diffusion into the substrate can prevent the successful preparation of well-ordered, stoichiometric, FePt nanoparticles. In this work we report the composition changes during annealing observed for small (<10 nm) FePt nanoparticles on thermally grown SiO_2 layers on Si wafer substrates. Additionally, we describe the use of a controlled reducing gas mixture, $Ar+H_2+H_2O$, to reduce the loss of Fe. © *2006 American Institute of Physics*.
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I. INTRODUCTION

FePt alloys consisting of the chemically ordered $L1_0$ phase are of interest for ultrahigh magnetic recording media applications due to the high magnetocrystalline anisotropy ($\sim 10^7 - 10^8$ ergs/cm^3) of this tetragonal crystal structure. Typically, the synthesis of ordered $L1_0$ FePt nanoscale materials involves the preparation of A1 (fcc) phase FePt thin film or nanoparticle samples, and subsequent annealing to allow the fcc to $L1_0$ phase transformation. During this process, control of the chemical stoichiometry should be maintained because of the strong dependence of the chemical order and uniaxial magnetic anisotropy on stoichiometry.[1–4] However, few reports have been published on the compositional stability during annealing of FePt nanoscale samples. Thomson *et al.* reported the formation of Fe silicides due to the high-temperature annealing for FePt thin films on a Si substrate, which caused a substantial drop in magnetization.[5] While thermally grown SiO_2 layers are commonly used with Si wafer substrates to prevent silicide formation, quantitative reports on the effectiveness of the SiO_2 layer to maintain sample stoichiometry are absent.

In this paper we report the compositional stability of FePt nanoparticles on SiO_2/Si substrates during annealing in a reducing gas, consider possible mechanisms of Fe loss, and describe a controlled reducing gas annealing that improves compositional stability. Analytical transmission electron microscopy (TEM) was used to quantify the compositions of FePt nanoparticles prepared on thin (31 nm) SiO_2 layers. A loss of Fe during annealing at 750 °C in 97% Ar+3% H_2 was observed. The diffusion of Fe into the SiO_2 layer and chemical reaction of Fe with the SiO_2/Si substrate were considered to be likely mechanisms for the Fe loss. The diffusion of Fe across the thermally grown SiO_2 layer was observed for a relatively thick (8 nm) FePt deposit on a thin SiO_2 layer. Annealing with a controlled reducing gas mixture of $Ar+H_2+H_2O$ was explored to reduce the loss of Fe during annealing. In the presence of the uncontrolled trace levels of water vapor expected during annealing, a high H_2 partial pressure can favor the formation of iron silicide, while a low H_2 partial pressure may allow the formation of iron oxide. Based on simple thermodynamic considerations, a ratio of H_2 partial pressure to that of H_2O between 1.0 and 2.4 should be maintained for maximum stability of FePt in the presence of SiO_2. FePt nanoparticles on thin SiO_2 (31 nm) have been so annealed and the stability of the stoichiometry confirmed by analytical TEM. We conclude that the loss of Fe into SiO_2/Si is a concern for the compositional stability of single layers of FePt nanoparticles during high-temperature annealing and that control of the annealing gas ambient can significantly improve compositional stability.

II. EXPERIMENT

The $Fe_{50}Pt_{50}$ deposits were prepared at room temperature by DC co-sputtering of Fe and Pt from elemental targets. The initial deposit was not a continuous film, rather a collection of nanoparticles and/or a discontinuous thin film. The base pressure of the sputtering system was in the 10^{-8} Torr range prior to the introduction of the Ar sputtering gas at a pressure of 3 mTorr and a flow rate of 20 SCCM (standard cubic centimeter per minute). The amounts of FePt deposited corresponded to thicknesses of 0.25, 2, and 8 nm. The 0.25-nm- and 8-nm-thick films were deposited onto oxidized Si(100) wafers with an oxide thickness of 31 nm, while that for 2-nm-thick film was more than 100 nm. Film compositions were calibrated by Rutherford backscattering spectrometry (RBS). The uncertainties in elemental concentrations were ±0.5 at. % for both the Fe and Pt.

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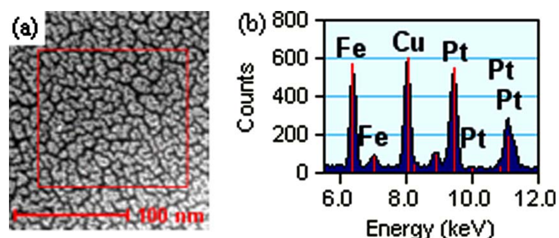


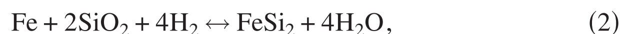
FIG. 1. TEM image and EDX spectrum of sample A. (a) HAADF image indicating region sampled and (b) EDX spectrum.

As is commonly done,[6] FePt nanoparticle samples were annealed at atmospheric pressure with a reducing gas flow to prevent the film from oxidizing. In our experiments a reducing gas of 97% Ar+3% H_2 was used for annealing of 750 °C for 20 h. While some trace levels of water vapor are expected to be present, the H_2O vapor pressure is not controlled and concentration in the gas flow is very low, and this procedure is referred to as an uncontrolled reducing gas annealing. For this annealing condition a loss of Fe can be observed for FePt nanoparticles, as described below.

Experiments using a more controlled reducing gas annealing condition were also performed. For these experiments, an intentionally higher and controlled H_2O vapor pressure was used in conjunction with the 97% Ar+3% H_2 reducing gas to reduce the possible formation of silicides, as well as oxides, during high-temperature annealing.

A thermodynamic model of the chemical reactions of Fe, Si, H, and O is described below to illustrate the advantages of a controlled reducing gas annealing for FePt nanoparticle processing. This very simplified model assumes that the Pt does not participate, that the Fe present is available as elemental Fe, that the available bulk thermodynamic data are representative of thin films, and that mixtures (e.g., $Si_1Fe_xO_y$) and other phases do not form. The reactions that are considered are the formation of an iron silicide with the reduction of SiO_2, Eqs. (1) and (2), and the formation of iron oxide by reaction with water vapor, Eq. (3). Qualitatively, in a strongly reducing ambient, the reduction of SiO_2 makes Si available and promotes the formation of FeSi, while in a nonreducing ambient water vapor is able to oxidize Fe and form FeO.

$$Fe + SiO_2 + 2H_2 \leftrightarrow FeSi + 2H_2O, \quad (1)$$



$$Fe + 2SiO_2 + 4H_2 \leftrightarrow FeSi_2 + 4H_2O, \quad (2)$$

TABLE I. FePt sample list, with as-deposited composition of $Fe_{50}Pt_{50}$.

			Annealing condition		
	Nominal FePt thickness (nm)	SiO_2 thickness (nm)	Temperature (°C)	Time (h)	Gas
Sample A	4	31	N/A	N/A	N/A
Sample B	0.25	31	750	20	Ar/H_2
Sample C	0.25	31	750	20	Ar/H_2/H_2O
Sample D	8	31	750	20	Ar/H_2
Sample E	2	>100	750	20	Ar/H_2

$$Fe + H_2O \leftrightarrow FeO + H_2. \quad (3)$$

Quantitative thermodynamic calculations using the data from Ref. 7 suggest that a ratio of H_2 partial pressure to that of H_2O between 1.0 and 2.4 should be maintained to prevent both silicide formation [reactions (1) and (2)] and oxide formation [reaction (3)]. Higher H_2 partial pressure favors the formation of iron silicide, while a lower H_2 partial pressure favors iron oxide formation. The possible reactions in our real FePt nanoparticle/substrate system are much more complex than allowed for by the simple model above. However, the ratio of H_2/H_2O calculated should represent a value appropriate for minimizing reactions between the nanoparticles and the substrate. For an annealing gas of Ar+3% H_2 gas at 1 atm, the desired range of H_2O partial pressure conveniently corresponds to the saturated vapor pressure of H_2O between 25 and 13 °C. Thus, a suitable H_2/H_2O partial pressure ratio is readily obtained by the use of a room-temperature water bubbler.

We have used both controlled and uncontrolled reducing gas annealing in our laboratory for a variety of investigations of FePt nanoparticles and report here on the characterization of five samples (identified as A, B, C, D, and E) by analytical TEM. The nominal FePt deposit thicknesses, SiO_2 membrane layer thicknesses, and annealing conditions for these samples are listed in Table I. The samples were analyzed using a Tecnai F30 TEM. Its energy dispersive x-ray (EDX) detector was used to determine the compositions of individual particles, and another detector, high-angle annular dark field (HAADF), was used for *Z*-contrast images.

III. RESULTS AND DISCUSSION

Figure 1 shows the HAADF image and EDX spectrum of the as-deposited 4-nm-thick $Fe_{50}Pt_{50}$ thin film (sample A). The integrated intensities of Fe K_α and Pt L_α peaks were used to determine the *K* factor of these two elements according to Cliff-Lorimer equation,[8] which gives a value of

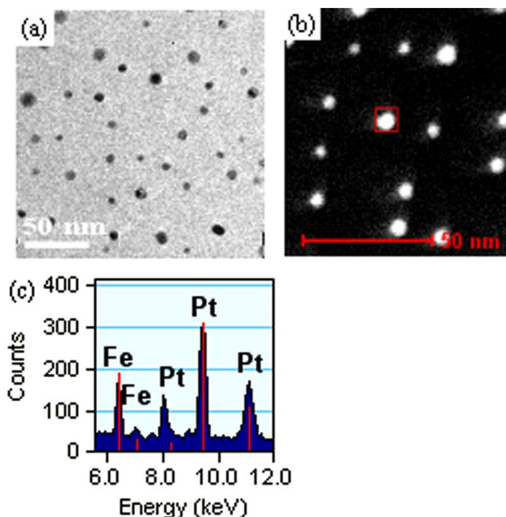


FIG. 2. TEM image and EDX spectrum of indicated individual FePt nanoparticle for sample B.

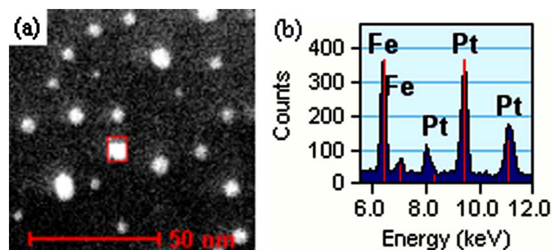


FIG. 3. TEM image and EDX spectrum of indicated individual FePt nanoparticle for sample C.

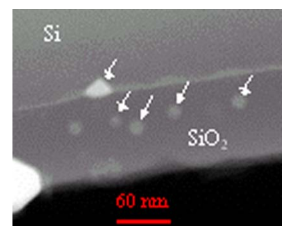


FIG. 4. Fe-rich precipitates (indicated by the arrows) appeared in SiO_2/Si substrate for sample D.

1.226±0.007. Based on this reference value, compositions of individual nanoparticles in annealed samples can be estimated from the corresponding EDX spectra.

The TEM images and EDX spectrum of FePt nanoparticles of sample B, a 0.25-nm-thick $Fe_{50}Pt_{50}$ thin film annealed in an uncontrolled reducing gas flow, are shown in Fig. 2. Well-isolated particles were achieved, as illustrated by Figs. 2(a) and 2(b). A typical EDX spectrum of one individual nanoparticle is exhibited in Fig. 2(c). The data fit results give a composition of $Fe_{33}Pt_{67}$, with uncertainties of ±5 at. % for Fe and ±6 at. % for Pt, respectively. More than ten particles with different sizes were examined. The compositions ranged from $Fe_{24}Pt_{76}$ to $Fe_{51}Pt_{49}$, with an average value of $Fe_{32}Pt_{68}$, and standard deviation of 9 at. % for both Fe and Pt.

To prevent the formation of iron silicides and oxides, annealing in a controlled reducing gas flow was performed on sample C, which was prepared in the same deposition experiment as sample B. Its HAADF image and a typical EDX spectrum are shown in Fig. 3. The data fit gives a composition of $Fe_{51}Pt_{49}$, with uncertainties of ±4 at. % for Fe and ±4 at. % for Pt. The range of compositions was found from $Fe_{47}Pt_{53}$ to $Fe_{52}Pt_{48}$ with an average value of $Fe_{51}Pt_{49}$, and a standard value of 2.1 at. % for both Fe and Pt.

To determine the mechanisms responsible for the loss of Fe during annealing in an uncontrolled reducing gas, an 8-nm-thick FePt film (sample D) was annealed under the same condition as sample B. The appearance of Fe-rich precipitates in the SiO_2/Si substrate layer, as shown in Fig. 4, suggested that the diffusion of Fe and chemical reaction of Fe with SiO_2/Si substrate can be considered as a likely mechanism for the loss of Fe from the FePt nanoparticles.

To examine the influence of SiO_2 thickness on the FePt composition stability, 2 nm FePt was deposited on a very thick SiO_2 (>100 nm) layer and was annealed in an uncontrolled reducing gas flow (sample E). In comparison to sample B, a similar loss of Fe was not detected in sample E. According to thermodynamic calculations, it is possible that Fe will react directly with SiO_2 in the presence of H_2 during high-temperature annealing. However, the reaction may be kinetically unfavorable due to a very low diffusivity or solubility of Fe in SiO_2.

IV. CONCLUSIONS

The loss of Fe due to oxidation or diffusion into the substrate can prevent the successful preparation of well-ordered, stoichiometric, FePt nanoparticles. In this work we report the composition changes observed for small (<10 nm) FePt nanoparticles on thermally grown SiO_2 layers on Si wafer substrates. For nanoparticles prepared on thin (31 nm) SiO_2 layers, a loss of Fe during annealing at 750 °C in Ar+3% H_2 was observed by analytical transmission electron microscopy (TEM). Probable factors contributing to this composition change were carefully examined. It was found that diffusions and chemical reactions of Fe and Si/SiO_2 substrates may be responsible for this change. A similar loss for nanoparticles on thicker (>100 nm) SiO_2 was not detected by EDX, but should not be presumed negligible. The diffusion of Fe across SiO_2 was confirmed for a relatively thick (8 nm) FePt deposit on the thinner SiO_2 by the observation of iron-rich precipitates within the Si wafer.

Wet annealing was explored to prevent the loss of Fe during annealing. Based on thermodynamic considerations, a ratio of H_2 partial pressure to that of H_2O between 1.0 and 2.4 should be maintained. FePt nanoparticles on thin SiO_2 (31 nm) have been so annealed and an improved stability of the stoichiometry was confirmed by analytical TEM. We conclude that the loss of Fe into SiO_2/Si is a concern for the compositional stability of single layers of FePt nanoparticles during high-temperature annealing and that control of the annealing gas ambient may improve compositional stability.

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