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Probing the A1 to L10 transformation in FeCuPt using the first order reversal curve method

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The A1-L10 phase transformation has been investigated in (001) FeCuPt thin films prepared by atomic-scale multilayer sputtering and rapid thermal annealing (RTA). Traditional x-ray diffraction is not always applicable in generating a true order parameter, due to non-ideal crystallinity of the A1 phase. Using the first-order reversal curve (FORC) method, the A1 and L10 phases are deconvoluted into two distinct features in the FORC distribution, whose relative intensities change with the RTA temperature. The L10 ordering takes place via a nucleation-and-growth mode. A magnetization-based phase fraction is extracted, providing a quantitative measure of the L10 phase homogeneity. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4894197]
non-equilibrium synthesis, and the magnetic phase fraction extracted by FORC is a convenient and complementary measure of the L1₀ ordering, which directly captures distributions in the relevant magnetic characteristics.

Atomic-scale multilayer films with nominal structure of [Fe(0.9 Å)/Cu(x)/Pt(1.4 Å)]₁₆ were grown by DC magnetron sputtering from elemental targets on amorphous SiO₂(200 nm)/Si substrates in a vacuum chamber with base pressure of 7 × 10⁻⁷ Torr. The Cu thickness (x) is varied to adjust the stoichiometric ratio (e.g., 0.4 Å for Fe₃₉Cu₁₆Pt₄₅). The introduction of Cu has been shown to selectively replace Fe atoms and help to tune the material properties to be desirable for HAMR applications. Subsequently the films were annealed by RTA at various temperatures (10 s rise + 10 s dwell time) in 1 × 10⁻⁵ Torr vacuum using infrared (IR) heating lamp with wavelength of 400–1100nm. Due to its small band gap of 1.1 eV, the Si substrate readily absorbed the IR light, in contrast to the amorphous SiO₂, which has a much larger 8.9 eV band gap. The thin FePt was mainly heated through thermal conduction across the SiO₂ barrier. As a result, the quick thermal expansion of the Si substrate exerts significant tensile stress on the atomic-scale multilayers of FePt across the SiO₂ and transfers the thermal energy to assist the L₁₀ ordering as well as (001) orientation of the films. After RTA the films were capped with a thin layer of Ti (20 Å) to prevent oxidation. For simplicity the rest of the paper will mainly focus on a series of Fe₃₉Cu₁₆Pt₄₅ samples (referred to as FeCuPt hereafter), while results from other samples are provided in the supplementary material.

X-ray diffraction was performed using a Bruker D8 thin film x-ray diffractometer with Cu Kα radiation, and used for phase identification following procedures outlined previously. Film microstructure and morphology were characterized by electron diffraction, transmission electron microscopy, and atomic force microscopy. Magnetic measurements were performed using vibrating sample magnetometry (VSM) at room temperature with the field applied perpendicular to the films, unless otherwise noted. To investigate detailed magnetization reversal, FORC measurements were performed as follows: From positive saturation the magnetic field was swept to a reversal field, back to positive saturation, tracing out a FORC. The process was repeated for decreasing HR until negative saturation was reached. The normalized FORC-distribution was then extracted, where MS is the saturation magnetization. Alternatively the FORC distribution could be represented in another coordinate system defined by local coercivity HC = (H − HR)/2 and bias field HB = (H + HR)/2.

XRD patterns for the Fe₃₉Cu₁₆Pt₄₅ films are shown in Fig. 1. For RTA temperatures TRTA < 350°C there are no appreciable FeCuPt peaks, indicating poor initial crystalline ordering. At TRTA ≥ 350°C, both (001) and (002) peaks are clearly observed. The presence of the (001) peak indicates the establishment of the L1₀ phase, as it is forbidden in the A1 phase. The order parameter S is calculated from the I₀₀₀₁/I₀₀₀₂ ratio to quantify the degree of L1₀ ordering, where I₀₀₀₁ and I₀₀₀₂ are the integrated intensity of the (001) and (002) peak, respectively, corrected for absorption, Lorentz factor, Debye-Waller factor, and angular dependent atomic scattering factors. The order parameter is normalized to the calculated maximum value, SMax = 1 − 2Δ, where Δ = 0.05 is the variation in the (FeCu):Pt atomic ratio from 50:50. The S/SMax is determined to be 1.0, 0.97, and 0.97 for TRTA of 350°C, 375°C, and 400°C, respectively, seemingly suggesting a high degree of L1₀ ordering at these temperatures.

However, at TRTA < 350°C, the absence of (001) or (002) peak makes it impractical to extract the L1₀ ordering parameter using this approach. The XRD order parameter is dependent on (I₀₀₀₁ + I₀₀₀₂)/(I₀₀₀₁ − I₀₀₀₂); the (001) peak is forbidden in the A1 phase, (I₀₀₀₁ + I₀₀₀₂) = 0, thus S/SMax will scale between 0 for the fully A1 phase to unity for the fully L1₀ phase. In the present case, no (002) peak is observed for the A1 phase, thus (I₀₀₀₁ + I₀₀₀₂) = 0, and S is only dependent on I₀₀₀₁/I₀₀₀₂, which is identical to SMax. Therefore S does not vary with the phase transformation and cannot be used in its usual context to measure the L1₀ ordering. More generally, when the sample’s initial crystalline ordering is non-ideal (e.g., the (002) intensity changes substantially during annealing), the order parameter S is no longer applicable in gauging the L1₀ ordering extent.
FIG. 1. X-ray diffraction patterns of Fe$_{39}$Cu$_{16}$Pt$_{45}$ thin films annealed by RTA at 300 °C–400 °C. The sharp (002) peak of the Si substrate is suppressed in some of the samples due to a slight deviation from the Bragg condition, which has no appreciable effect on the FeCuPt peaks.

Transmission electron microscopy (TEM) and electron diffraction show that all samples have crystalline grains (see the supplementary material$^{23}$); at $T_{\text{RTA}} = 325$ °C, both rounded and elongated grains are observed, with an average size of $\sim 6$ nm; at $T_{\text{RTA}} = 400$ °C, only elongated grains are observed, with an average size of $\sim 12$ nm, which are consistent with the effects of the tensile stress during the RTA. It is the crystalline nature of the films that allows us to use the conventional $S$ parameter to gauge the degree of ordering. Cross-sectional TEM studies on a similar series of Fe$_{52}$Pt$_{48}$ samples (i.e., Cu content is zero) illustrate that during the phase transformation, residual disordered A1 regions exist only in certain parts of the otherwise (001) oriented L1$_0$ films (Fig. 2), rather than homogeneous dispersion over numerous sites throughout the films. However, it is difficult to quantify the L1$_0$ phase fraction from TEM alone.

Room temperature hysteresis loops in the out-of-plane (OOP) and in-plane (IP) geometries for the Fe$_{39}$Cu$_{16}$Pt$_{45}$ samples annealed by RTA at 300 °C–400 °C are shown in Fig. 3. After RTA at 300 °C and 325 °C, the OOP major loops are nearly closed with negligible remanence, while the IP loops are sharp with large remanence and small coercivity, indicating an out-of-plane hard axis and suggesting that the films are primarily in the low anisotropy A1 phase. As the RTA temperature $T_{\text{RTA}}$ is increased to 350 °C, the OOP loop shows a gradual increase in remanence and coercivity, still showing largely hard-axis behavior, while the IP loop shows a sudden increase in coercivity and decrease in remanence. A more distinct change is observed for RTA at 375 °C and 400 °C, where the OOP loop exhibits easy-axis behavior with remanence approaching unity and a much enhanced coercivity,$^{25}$ and the IP loop has the smallest remanence, suggesting the film is primarily L1$_0$ ordered with out-of-plane anisotropy. The $T_{\text{RTA}}$-dependent remanence, coercivity, and saturation...
FIG. 3. Room temperature hysteresis loops in the (a) out-of-plane and (b) in-plane geometries of Fe$_{39}$Cu$_{16}$Pt$_{45}$ thin films annealed by RTA at 300 $^\circ$C–400 $^\circ$C. Trends for the (c) coercivity and remanence and (d) saturation magnetization are also included.

magnetization are shown in Figs. 3(c) and 3(d). The continuous changes of the remanence and coercivity illustrate a gradual evolution of the A1-L$_{10}$ phase transformation with increasing $T_{\text{RTA}}$.

To further investigate the A1-L$_{10}$ phase transformation and the magnetization reversal behavior of the films, FORCs have been measured in the OOP geometry for the Fe$_{39}$Cu$_{16}$Pt$_{45}$ samples. For $T_{\text{RTA}}$ of 300 $^\circ$C, the family of FORCs is highly compressed inside the slanted major loop [Fig. 4(a)]. The corresponding FORC distribution $\rho(H_C, H_B)$ shows a single vertical ridge located near $H_C = 0$ [Figure 4(b)], which is clearly seen in the normalized projection of $\rho(H_C, H_B)$ onto the $H_C$ axis ($dM/dH_C$) [Figure 4(c)]. These characteristics show that the magnetization is largely reversible and the coercivity is small, indicating that the sample is in the low anisotropy A1 phase.

For $T_{\text{RTA}}$ of 325 $^\circ$C and 350 $^\circ$C, the family of FORCs fills the slanted hard-axis major loop with higher remanence and larger coercivity, indicating an increasing degree of irreversibility [Figures 4(d) and 4(g), respectively]. In the FORC distributions, the vertical ridge near $H_C = 0$ is still the most outstanding feature; interestingly, a second horizontal FORC feature located at a higher $H_C$ of $\sim$2.8 kOe begins to emerge at 325 $^\circ$C [Figures 4(e) and 4(f)] and becomes quite appreciable at 350 $^\circ$C [Figures 4(h) and 4(i)]. These features demonstrate that the L$_{10}$ ordering is beginning to occur, however, the A1 phase is still the majority phase that dominates the magnetization reversal.

For $T_{\text{RTA}}$ of 375 $^\circ$C and 400 $^\circ$C, the family of FORC’s show qualitatively different easy-axis behavior [Figures 4(j) and 4(m)]. In the FORC distribution, the vertical ridge near $H_C = 0$ has largely vanished and the horizontal FORC feature has become quite prominent, with its center shifting to higher $H_C$ values [$H_C = 3.2$ kOe in Figures 4(k) and 4(l) for 375 $^\circ$C, and 3.7 kOe in Figures 4(n) and 4(o) for 400 $^\circ$C]. These samples exhibit essentially full L$_{10}$ ordering and the disappearance of the A1 phase.
FIG. 4. Family of FORC’s (top row), corresponding FORC distributions (middle row) and their normalized projections \(\frac{dM}{dH_C'}\) onto the local coercivity \(H_C\) axis (bottom row) for Fe_{39}Cu_{16}Pt_{45} samples annealed at 300 °C (a)–(c), 325 °C (d)–(f), 350 °C (g)–(i), 375 °C (j)–(l), and 400 °C (m)–(o).

The two distinct FORC features directly correspond to the low and high anisotropy A1 and L1_0 phase, respectively. Their coexistence at intermediate \(T_{RTA}\) of 325 °C and 350 °C, while the major loop only shows the hard-axis reversal, demonstrates the capability of FORC in deconvoluting magnetic phases. Furthermore, the evolution of these two FORC features under increasing \(T_{RTA}\) reveals details of the A1-L1_0 phase transformation mechanism. The fact that these two features remain well separated in the FORC distribution (in \(H_C - H_B\) coordinates), and their relative intensity changes under increasing \(T_{RTA}\), is indicative of a nucleation-and-growth mechanism of the L1_0 phase. Under this mechanism, annealing changes the relative ratios of the magnetically hard and soft phases, primarily modifying the intensity of the corresponding FORC features. This is consistent with the TEM image shown in Figure 2, which illustrates certain residual A1 “pockets” in the matrix of L1_0 films. Alternatively, had the phase transformation with \(T_{RTA}\) been realized through a uniform growth mode, we would have expected a gradual shift of a single FORC feature as a whole, from low to high coercivity, and more extensive A1 regions in the TEM view. Thus the FORC technique is able to uniquely identify and separate contributions from the hard and soft phases, despite the single phase appearance of the major loop.

Furthermore, the integration \(I_{irrev} = \int \rho(H_B, H)dH_BdH = \int \rho(H_B, H_C)dH_BdH_C\) for \(H \geq H_R\) captures the total amount of irreversible magnetic switching in a sample. Thus, it can be used to quantitatively determine the amount of magnetic phases. By selectively integrating the normalized FORC distribution (Eq. (1)) over the horizontal feature corresponding to the L1_0 phase, compared to the saturation magnetization of the entire sample, we can extract a magnetization-based L1_0 phase fraction. Since the saturation magnetization of the A1 (818 emu/cm^3) and L1_0 (790 emu/cm^3) phases are nearly identical, the magnetic phase fraction can be directly correlated to the structural phase fraction. In addition, it is possible to reconstruct the major hysteresis loops of each phase.

The evolution of the L1_0 phase fraction in Fe_{39}Cu_{16}Pt_{45} determined by FORC with \(T_{RTA}\) is shown in Fig. 5, indicating a gradual increase in the L1_0 ordering up to 350 °C, followed by an abrupt ordering near 375 °C. This is consistent with the kinetic ordering temperature reported earlier. For comparison, the XRD order parameters are also included in Figure 5, which show good agreement only for highly L1_0 ordered 400 °C sample. Similar trends are also found in another series of Fe_{28}Cu_{27}Pt_{45} films (see the supplementary material). While the structural order parameter is not always readily available (such as the case here for the 300 °C and 325 °C samples) or reliable (depending on capturing the proper crystal planes of the A1 phase), the magnetization-based phase fraction provides a complementary and direct measure of the L1_0
phase homogeneity, which is critical to SFD and eventual application of such materials in HAMR media.

In conclusion, we have investigated the $A_1$-$L_{10}$ phase transformation in (001) FeCuPt thin films prepared by a non-equilibrium strain-assisted synthesis approach. The $A_1$ and $L_{10}$ phases manifest themselves as two distinct features in the FORC distribution, whose relative intensities change as the RTA temperature increases from 300 °C to 400 °C. The $L_{10}$ ordering takes place via a nucleation-and-growth mode. Traditional x-ray diffraction suggests an unrealistic order parameter due to poor initial crystalline ordering of the $A_1$ phase. An alternative magnetization-based $L_{10}$ phase fraction is extracted. The FORC method not only sheds insight into the $L_{10}$ ordering mechanism in these ultrathin films, but also provides a quantiative measure of the $L_{10}$ phase homogeneity. This approach is applicable to other $L_{10}$ materials such as MnAl$^{33}$ and MnGa$^{34}$ that are being keenly pursued for rare-earth-free permanent magnets, as well as magnetic phase separation studies in general.

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