Influence of the antiphase domain distribution on the magnetic structure of magnetite thin films

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A long-range ordered magnetic domain structure was found in magnetitelike ($Fe_{3-\delta}O_4$, $\delta \approx 0.03$) thin films prepared by molecular beam epitaxy on MgO (100) substrates. The stripelike magnetic domain structure arising after suitable postprocessing differs significantly from earlier observations. The field-dependent domain structure was investigated by magnetic force microscopy in external magnetic fields. The magnetic domain structure results from a moderate perpendicular anisotropy. The domain structure is pinned, and the pinning centers arise from the magnetite antiphase domain structure. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2356308]

Fe_3O_4 (magnetite) thin films belong to the most intensively studied epitaxial ferrite films and have received recent interest because of the half metallicity and full spin polarization.[1] These unique properties make Fe_3O_4 thin films a candidate for magnetic tunnel junctions and spin-valve devices.[1–3] However, the observed magnetic properties of Fe_3O_4 films are puzzling.[4,5] An unexpectedly low efficiency of Fe_3O_4 multilayer spin valves was found.[6] Conversion electron Mössbauer spectroscopy[4,5] (CEMS) and nuclear resonance data[7] reveal a notable fraction of magnetic moments pointing out of the film plane, while an in-plane orientation would be expected from the interplay of crystalline, magnetoelastic, and shape anisotropies.[4] The films are still unsaturated at 7 T, whereas the magnetization is expected from the anisotropy to be saturated at much lower field values.[4] These unexpected properties appear to be independent of the employed deposition methods and have been related to antiphase boundaries (APBs) existing in epitaxial films.[5] For Fe_3O_4 grown on MgO, the lattice constant of the film is twice that of the substrate. This results in stacking faults in the cation sublattice forming the APBs. In particular, across some types of APBs, a strong antiferromagnetic coupling is expected. A quantitative estimate of the amount of APBs with antiferromagnetic coupling was obtained from a transmission electron microscopy (TEM) analysis of the various types of APBs present in a given sample.[8] APBs with antiferromagnetic coupling pin the domains' magnetization nearby in opposite directions, even in a relatively high external magnetic field.[7] Magnetic force microscopy (MFM) has been previously employed to investigate the domain structure related to APBs.[9–12] Most of the results show magnetic domain structures with a 100–300 nm characteristic length scale. This is considerably larger than the average size of APBs as mapped by TEM.[8,13] However, the irregularly shaped magnetic structures so far prevented a deeper understanding of the micromagnetism of magnetite films.

From the application point of view, it would be most convenient if the magnetic properties of magnetite thin films resemble those of the bulk material. Recently, it was shown that the additional annealing in air subsequent to an ultrahigh-vacuum annealing has a strong influence on the magnetic properties of samples. Such a treatment results in an increase of the magnetization at 1 T by 14% and in a decrease of coercive fields by 40% with respect to as-grown samples.[14] Annealing in air, however, was always questioned because of uncontrolled film oxidation. For the present study, we used magnetite films prepared in the same way as described in Ref. 14 and measured deviations from stoichiometry by means of CEMS. Fits to the spectra shown in Fig. 1(c) indicate a 58% reduction in the relation between mixed valence iron to trivalent iron, $\beta = Fe^{2.5+}/Fe^{3+}$, by 4 min annealing in air. From the relation $\delta = (2-\beta)/(6+\beta)$, a composition of $Fe_{(3-\delta)}O_4$ with $\delta = 0.03 \pm 0.01$ is obtained for the

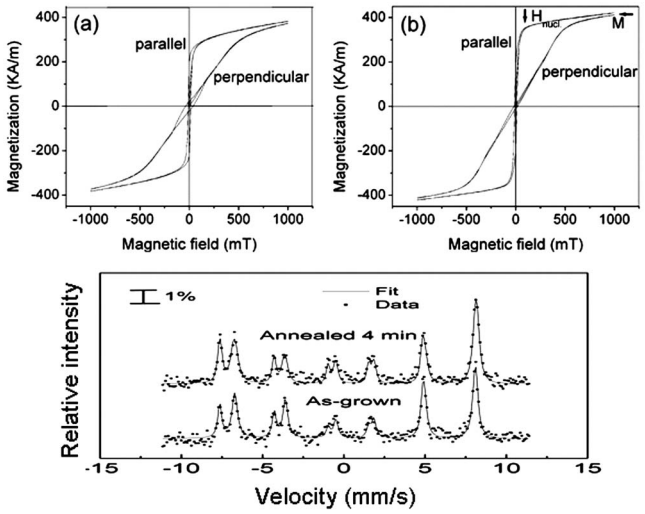

FIG. 1. Magnetization curves of (a) as-grown and (b) annealed Fe_3O_4 films for in-plane (parallel) and out-of-plane (perpendicular) magnetic fields. In-plane nucleation field and approximate saturation magnetization are indicated by arrows. (c) CEMS spectra of as-grown and annealed Fe_3O_4 films.

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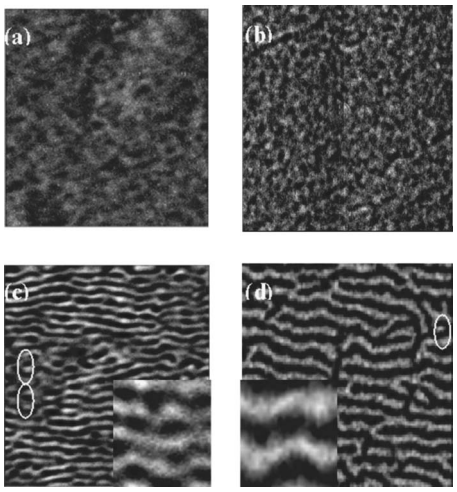

FIG. 2. MFM images of as-grown and annealed Fe_3O_4 films. (a) and (b) are images of as-grown Fe_3O_4 films of 100 and 400 nm thicknesses, respectively. (c) and (d) are the corresponding images of the films annealed for 4 min in air. The image size is 6×6 μm^2. The size of the insets is 1×1 μm^2. Individual dots in (c) and (d) are marked by circles.

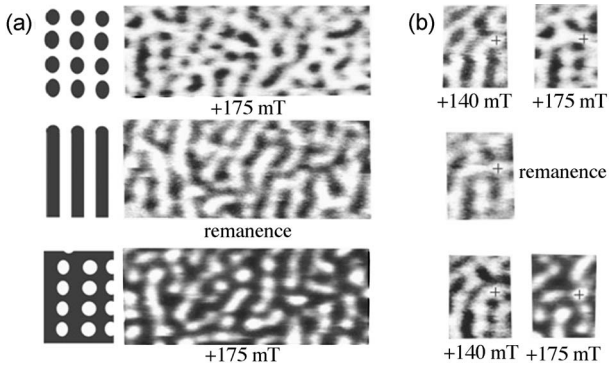

FIG. 3. Domain structures in an external perpendicular magnetic field. (a) Overall behavior together with schematic representation. The size of the images is 4×1.5 μm^2. (b) Behavior of a single dot marked by the cross.

annealed film. As-grown samples show a perfect stoichiometry. The high stoichiometric resolution was obtained by measuring over several weeks. The increased magnetization at 1 T after annealing [see Figs. 1(a) and 1(b)] cannot be caused by γ-Fe_2O_3 inclusions, which are formed from Fe_3O_4 via oxidation. γ-Fe_2O_3 has a smaller saturation magnetization of 392 A/m compared to 470 A/m for Fe_3O_4. The change in the magnetization at 1 T is rather related to chemical modification of APBs during short annealing.[14] We have also performed careful studies utilizing Raman spectroscopy and a high-resolution triple-axis x-ray diffractometer (XRD). The films after annealing show no evidence of a second phase. They are fully strained without misfit dislocations.

In the following, we present MFM results for molecular beam epitaxy grown Fe_3O_4 thin films with and without annealing treatment. The magnetization curves in Figs. 1(a) and 1(b) are similar in their broad features. In-plane coercive fields are low and the saturation fields are very high. For both in-plane and out-of-plane fields, saturation is not achieved at 1 T. However, the magnetization at 1 T is larger for the annealed sample.

Commercial Si cantilevers with 30 nm CoCr magnetic coating were employed for MFM measurements. From imaging of reference samples, these tips were known to be sensitive to the out-of-plane component of the magnetic stray field of the sample.

Figures 2(a) and 2(b) show MFM images of as-grown Fe_3O_4 thin films of 100 and 400 nm thicknesses, respectively. Irregular domain structures similar to those in these images have been observed before.[9–12] MFM images of the same Fe_3O_4 films after annealing for 4 min in air at 250 °C are shown in Figs. 2(c) and 2(d). Upon annealing, a long-range ordered stripelike magnetic domain structure has developed. The stripe domains exhibit some disorder at a smaller scale than the domain size. The insets in Figs. 2(c) and 2(d) show the detailed structure of the stripe domains. Along with stripe domains, there are still some individual dots as marked in Figs. 2(c) and 2(d).

In Fig. 3(a), a perpendicular field was applied. In a field of 175 mT, the dark stripe domains are partly transformed into dots. For an opposite field, the same occurs for the bright domains. A closer analysis of the magnetization reversal process confirms that the vast majority of dots are immobile. As a representative example, Fig. 3(b) shows the immobility of a single dot upon magnetization reversal.

Stripe domains in an essentially in-plane magnetized film have been observed before in Permalloy,[15] cobalt,[16] and iron[17] films. In such films, there is a perpendicular anisotropy that is smaller than the shape anisotropy. The magnetization in the respective weak stripe domains is tilted at alternating directions from the film surface.[15] In an external perpendicular field, weak stripe domains are transformed into bubble domains, as observed in Ref. 16. The same process is evident from Fig. 3, where the immobile dots correspond to the bubble domains. A minimum film thickness of t_{min} is required for weak stripe domains to occur. We did not observe any stripe domains for a thickness of 20 nm. For $t>t_{min}$, the domain size is expected to scale with the square root of the film thickness.[15] Domain sizes and thicknesses of the two films in Fig. 2 roughly follow this law. According to the theory, domains nucleate and develop into the stripe pattern upon reducing a saturating in-plane field. The stripes are preferentially oriented along the field direction. Our result agrees well with the theoretical predictions. The nucleation field is related to the perpendicular magnetic anisotropy and the minimum film thickness t_{min}. This relation yields a perpendicular anisotropy[15] of $K=\mu_0 M H_{nucl}/\{2[1-(t_{min}/t)^{2/3}]\} \approx 5.7\times10^4$ J/m^3.

The magnetization M within domains and the nucleation field $\mu_0 H_{nucl}$ are taken from the in-plane magnetization curve [Fig. 1(b)]. The values are 420 kA/m and 100 mT, respectively. The film thickness t is 100 nm. The MFM images show that 20 nm$<t_{min}<$100 nm. Assuming $t_{min}=50$ nm for simplicity, one obtains an anisotropy of about one-half of the shape anisotropy, given by $\mu_0 M^2/2=1.1\times10^5$ J/m^3. This is about five times larger than the crystalline anisotropy of bulk Fe_3O_4, i.e., 1.1×10^4 J/m^3.[4] The MFM data imply that an additional perpendicular anisotropy is induced by a few minutes of annealing in air. This is confirmed by CEMS data. A measure of in-plane orientation is given by the p parameter. For a film with homogeneous magnetization, $p=2\sin^2\theta/(1+\cos^2\theta)$, θ being the angle between the magnetization and the surface normal. The p value changes from 1.2 to 0.8 after annealing. $p=2$ corresponds to an in-plane moment alignment and $p=0$ to a perpendicular alignment.

XRD data from Ref. 14 show that the increase of strain is only a tenth of the strain value prior to annealing. Thus,

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the increase in strain cannot be responsible for a perpendicular anisotropy that is sufficient to generate stripe domains.

Properties of as-grown $Fe_{3-\delta}O_4$ films on MgO have been studied in Ref. 18. For $\delta < 0.2$, no indication of an increase of perpendicular anisotropy with increasing δ was found. The data rather point toward a decreasing anisotropy.

The APBs with antiferromagnetic coupling are directly associated with a strong out-of-plane component of the magnetization.[19] Chemical modification of APBs during a short annealing is able to change the magnetic properties of Fe_3O_4 films substantially, even without a notable increase of the antiphase domain size.[14] Thus, chemical modification occurring in APBs during annealing in air is a possible origin for the perpendicular anisotropy. The appearance of the domain structure is possibly caused by a change in the magnetic domain wall energy. The weak stripe domain pattern is the result of a competition between the perpendicular anisotropy and the domain wall energy.

The observed domain structure is locally disordered and involves pronounced pinning to the crystal lattice: The small-scale disorder displayed in Figs. 2(c) and 2(d) is likely to be caused by crystalline defects. From Fig. 2, one obtains a length scale for the domain disorder of some tens of nanometers. This is comparable to the expected size of APBs.[13] From XRD and CEMS measurements, it can be concluded that misfit dislocations and stoichiometric defects do not play a dominant role. As APBs are thus the only types of defects present in the film with a sufficient density, it is reasonable to relate local magnetic disorder and pinning to an antiferromagnetic coupling across APB.

In summary, a stripelike magnetic domain structure has been found in Fe_3O_4 thin films annealed in air. The magnetization is predominantly in plane. However, small out-of-plane components form the observed stripes. The variation of the magnetic structure in external magnetic fields is well explained as weak stripe domains. Domains are strongly pinned by structural defects related to APBs. The appearance of the domain structure is due to the annealing procedure. Chemical modification of APBs during annealing is a possible origin of the perpendicular anisotropy. The appearance of the domain structure points to a moderate perpendicular anisotropy or, alternatively, to a change in the magnetic domain wall energy.

Magnetite films have been considered for spin-valve applications. Here, soft magnetic layers are required with low coercivity and high saturation magnetization. The complex and persistent magnetic structure resulting from antiferromagnetic coupling across APBs is an obstacle to such kind of applications. On most substrates, APBs cannot be avoided. Annealing in UHV can only reduce the APB density. Subsequent partial oxidation is able to magnetically deactivate the APB to a certain degree. As a consequence, magnetization is approaching saturation much faster, i.e., the film becomes softer. We showed that partial oxidation also leads to a regular domain structure which is generally unwanted in spin-valve applications. However, film properties would rather be improved if antiferromagnetic coupling is reduced by deactivating the APBs while avoiding a perpendicular anisotropy. Alternative ways to chemically modify APBs are needed, such as ion bombardment or other means of modifying the interface at an atomic scale.

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