AIP Journal of Applied Physics

Perpendicular magnetic anisotropy in epitaxially strained cobalt-ferrite (001) thin films

H. Yanagihara, Y. Utsumi, T. Niizeki, J. Inoue, and Eiji Kita

Citation: Journal of Applied Physics **115**, 17A719 (2014); doi: 10.1063/1.4864048
View online: http://dx.doi.org/10.1063/1.4864048
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/115/17?ver=pdfcov
Published by the AIP Publishing

Perpendicular magnetic anisotropy in epitaxially strained cobalt-ferrite (001) thin films

H. Yanagihara,[a)] Y. Utsumi, T. Niizeki,[b)] J. Inoue, and Eiji Kita
Institute of Applied Physics, University of Tsukuba, Tsukuba 305-8573, Japan

(Presented 5 November 2013; received 23 September 2013; accepted 4 November 2013; published online 7 February 2014)

We investigated the dependencies of both the magnetization characteristics and the perpendicular magnetic anisotropy of $Co_xFe_{3-x}O_4$(001) epitaxial films ($x = 0.5$ and 0.75) on the growth conditions of the reactive magnetron sputtering process. Both saturation magnetization and the magnetic uniaxial anisotropy constant K_u are strongly dependent on the reactive gas (O_2) flow rate, although there is little difference in the surface structures for all samples observed by reflection high-energy electron diffraction. In addition, certain dead-layer-like regions were observed in the initial stage of the film growth for all films. Our results suggest that the magnetic properties of $Co_xFe_{3-x}O_4$ epitaxial films are governed by the oxidation state and the film structure at the vicinity of the interface. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4864048]

I. INTRODUCTION

Magnetic anisotropy (MA) is one of the most important properties of magnetic materials. In general, spin-orbit coupling is a primary source of origin of MA; and therefore, a large spin-orbit coupling constant and/or large orbital moments are often observed in strong MA materials.[1] It has been known that bulk cobalt ferrite possesses an exclusively large cubic MA of the order of $\approx 10^6$ erg/cm^3 among cubic spinel ferrites, and further, it exhibits remarkably large values of the magnetostriction constants.[2] Thin-films of cobalt-ferrites are expected to exhibit large perpendicular magnetic anisotropy (PMA) when substrate-induced lattice distortions couple to the large magnetostriction.[3,4] In the distorted films, the Co^{2+} ions located at the B-sites of the spinel structure probably acquire non-quenched orbital moments[5] like that in the bulk.[6–8] Again, MAs are mainly supposed to originate from the considerably large orbital moments of the Co^{2+} ions through the spin-orbit interaction. However, in cobalt-ferrite thin-films magnetic properties, such as MA and magnetization, are strongly dependent on the film-preparation methods and conditions.[5,9–13] Therefore, the potential for spintronics/magnetics of the cobalt-ferrite films is unknown and even the mechanism of the PMA is not clarified yet. Thus, it is important to determine the optimum growth conditions for the cobalt ferrite films to understand the mechanism of PMA.

Although there are several reports on the magnetic properties of epitaxial cobalt-ferrite thin films grown by various different methods, such as reactive molecular beam epitaxy,[10–12,14] pulsed laser deposition,[9,13] and sputtering,[15] most of the films grown by these methods exhibit remarkably lower saturation magnetization (M_S) than that of the bulk material. We recently determined that reactive sputtering appears to be an appropriate method to prepare spinel-type iron oxide ($Fe_{3-\delta}O_4$) films such as Fe_3O_4(001) and γ–Fe_2O_3(001) grown on MgO (001) substrates. The M_S values of the Fe_3O_4(001) and γ–Fe_2O_3(001) films are comparable with that of the bulk material. Based on our previous knowledge regarding $Fe_{3-\delta}O_4$ film growth, we have also found that $Co_xFe_{3-x}O_4$ epitaxial films with $x = 0.75$ grown on MgO(001) exhibit strong uniaxial PMA of the order of 10 Merg/cm^3 and large M_S values comparable with that of bulk material.[16]

In general, optimizing the growth conditions for reactive magnetron sputtering even with a single alloy target is complicated. These conditions include (i) growth temperature (substrate temperature), (ii) sputtering power, (iii) process pressure, and (iv) oxygen-gas flow rate among others. Since the number of parameters concerning sputtering conditions is so large, the growth conditions cannot be easily optimized. The optimized growth conditions are also possibly dependent on the composition of cobalt ferrites. In this paper, we report on the magnetic properties of cobalt ferrite epitaxial films with two different compositions grown on MgO (001) substrates under different conditions as a function of oxygen pressure. The results of our study provided two significant findings. First, the magnetic properties of $Co_xFe_{3-x}O_4$ films are dependent on the oxygen pressure during the sputtering process. Second, the $Co_xFe_{3-x}O_4$ films initially exhibit considerably lower magnetization values even under optimal conditions.

II. EXPERIMENTAL

Thin films of two different composition ratios of $Co_xFe_{3-x}O_4$(001) ($x = 0.5$ and 0.75) were grown epitaxially on cleaved MgO (001) substrates via the reactive rf magnetron sputtering technique using 2-in.-diameter Co-Fe alloy targets with the desired compositions of $Co_{0.17}Fe_{0.83}$ and $Co_{0.25}Fe_{0.75}$. Prior to film growth, MgO (001) substrates were annealed at 400 °C for 30 min. The process gas used was a mixture of Ar and O_2. The flow rate of Ar was fixed at 20.0 sccm corresponding to a partial pressure of ≈ 0.5 Pa,

[a)]Electronic mail: yanagiha@bk.tsukuba.ac.jp.
[b)]Present address: Advanced Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Sendai 980-8577, Japan. Electronic mail: t-niizeki@imr.tohoku.ac.jp.

whereas that of O_2 (ϕ_{O_2}) was varied from 4.0 to 10.0 sccm as a growth parameter. Under this condition, the O_2 pressure increases by $\approx$0.1 Pa during the sputtering process. The growth temperature was maintained at 300 °C and the rf-power of the sputtering process was set at 100 W. The other details of the growth conditions can be found in our previous work on epitaxial $Fe_{3-\delta}O_4$ films.[17] The surface structures were observed by reflection high-energy electron diffraction (RHEED) immediately after $Co_xFe_{3-x}O_4$ growth. The film thicknesses were determined via the x-ray reflectivity (XRR) technique using a conventional $\theta/2\theta$ diffractometer. All the magnetic measurements were carried out at room temperature (RT). The magnetization was measured using a superconducting quantum interference device, SQUID-VSM (Quantum Design, MPMS) at fields up to $\pm$70 kOe. The MAs were evaluated from the magnetic torque curves measured over the range of 0–90 kOe by a torque magnetometer (Quantum Design, PPMS Tq-Mag). The typical sample dimension was less than 2.0×2.0 mm^2 and the samples were shaped as squares.

III. RESULTS AND DISCUSSION

Figure 1 shows the typical RHEED images of the MgO (001) substrate and 40-nm-thick $Co_xFe_{3-x}O_4$(001) ($x = 0.5$) film grown under the condition of $\phi_{O_2} = 7.0$ sccm at a substrate temperature of 300 °C. Clear streaks and Kikuchi lines can be observed in both surface images, indicating that the surface is sufficiently flat and the crystalline quality of the film is good. In the image corresponding to $Co_xFe_{3-x}O_4$, there are additional streaks between those corresponding to MgO (001), indicating that the lattice unit of $Co_xFe_{3-x}O_4$ is approximately twice the lattice-unit size of MgO. Here, we remark that our x-ray-diffraction analysis revealed that the $Co_xFe_{3-x}O_4$ films were coherently grown on MgO (001) substrates with an in-plane lattice constant that was just twice that of MgO.[16] The crystal lattice of the $Co_xFe_{3-x}O_4$ films grown on MgO(001) is definitely strained with in-plane stretched stress.

The results of the typical magnetization measurements at RT are shown in Fig. 2. Finite remanences are observed in the *MH*-loops under the application of an out-of-plane magnetic field, while no remanence appears in the in-plane *MH*-loops, indicating that the $Co_xFe_{3-x}O_4$(001) films grown on MgO(001) are perpendicularly magnetized films. Since the M_S values of most of the previously reported $Co_xFe_{3-x}O_4$ films are significantly less than that of the bulk material, the

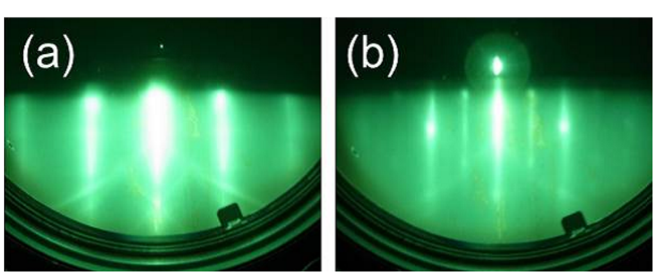

FIG. 1. RHEED images of (a) MgO(001), and (b) $Co_xFe_{3-x}O_4$ ($x = 0.5$) samples in [100] azimuth.

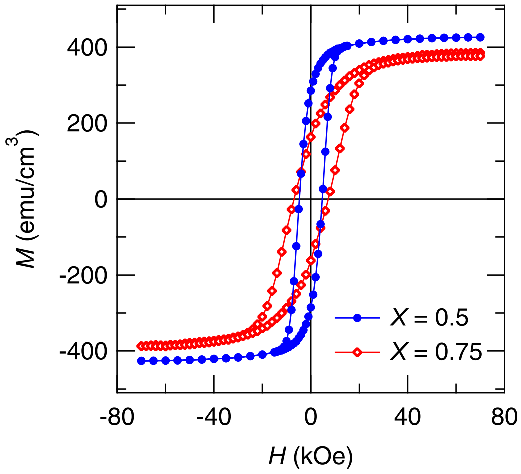

FIG. 2. Out-of-plane *MH*-loops for $Co_xFe_{3-x}O_4$ films with $x = 0.5$ and $x = 0.75$. The film thicknesses for $x = 0.5$ and $x = 0.75$ are 50 nm and 49 nm, respectively.

M_S value can be a good criterion to optimize the growth condition. In fact, M_S is strongly dependent on ϕ_{O_2} for all composition ratios, and some of the samples exhibit M_S values close to the bulk value of $Co_xFe_{3-x}O_4$.

In order to examine the thickness dependence of the M_S values of the $Co_xFe_{3-x}O_4$ films, the product of M_S and thickness t was plotted against t (see Fig. 3). Each value of M_St was obtained by dividing the measured magnetic moment by the area of the film. The thickness values were determined by the oscillation periods observed in the XRR results. In this plot, the slopes correspond to the M_S values, and the horizontal-axis intercept suggests the existence of a *dead layer*. From Fig. 3, we note that most of the $Co_xFe_{3-x}O_4$ films show a linear behavior, meaning that the M_S values determined in this manner are reasonably accurate. Although the M_S values for $x = 0.75$ appears dependent on the ϕ_{O_2} that for $x = 0.5$ is almost constant with respect to ϕ_{O_2}. It is to be noted that there are finite horizontal-axis intercepts for all samples with different values of x and ϕ_{O_2}. The typical value of the intercepts approximately ranges as 2-3 nm, suggesting that the *dead layer* or the region of smaller M_S exists in the initial growth stage. When spinel ferrite films are grown on the surfaces of non-spinel structures, such as MgO or $SrTiO_3$

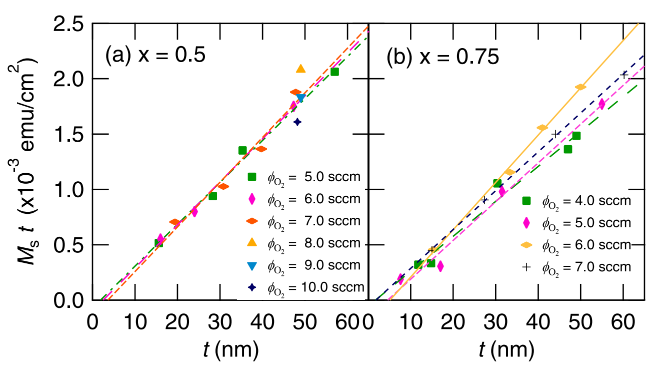

FIG. 3. Thickness dependence of M_S for (a) $x = 0.5$ and (b) 0.75. The vertical and horizontal axes correspond to the $Co_xFe_{3-x}O_4$ film thickness t and the product of the saturation magnetization and the thickness (M_St). Straight lines indicate the results of linear regression.

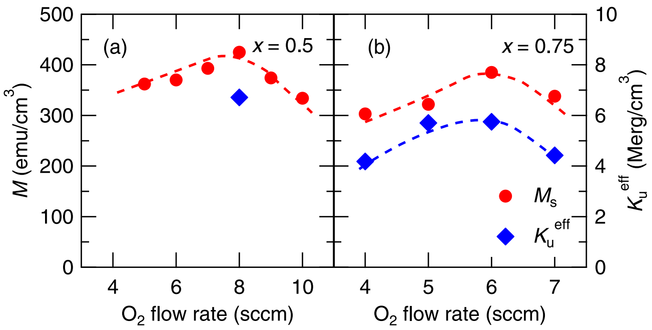

FIG. 4. Oxygen flow-rate dependence of M_S (circles) and K_u (diamonds) of $Co_xFe_{3-x}O_4$ with different composition ratios ($x = 0.5, 0.75$). Broken lines serve as visual guides.

substrates, a considerable number of anti-phase boundaries (APBs) emerge, as reported for Fe_3O_4 (001) films grown on a MgO (001) substrate. The formation of high-density APBs results in a corresponding reduction in M_S and/or high-field finite susceptibility.[18]

Figure 4 shows the ϕ_{O_2} dependence of the M_S and K_u values of $Co_xFe_{3-x}O_4$(001) for different values of x. For $x = 0.5$, the trend of $M_S(\phi_{O_2})$ exhibits a maximum at around $\phi_{O_2} = 8.0$ sccm, and the maximum M_S is approximately 430 emu/cm^3 that is comparable with the bulk value. On the other hand, $M_S(\phi_{O_2})$ reaches a maximum of ≈400 emu/cm^3 at around $\phi_{O_2} = 6.0$ sccm for $x = 0.75$. Moreover, the trend indicates that the larger-M_S samples exhibit larger K_u.

Here, we consider how ϕ_{O_2} affects the magnetic properties of $Co_xFe_{3-x}O_4$ films. According to our previous report on the epitaxial film growth of $Fe_{3-\delta}O_4$ ($0 \le \delta \le \frac{1}{3}$) by using the reactive magnetron sputtering technique, ϕ_{O_2} directly affects the sputtering mode.[17] We noticed that the presence of a threshold ϕ_{O_2} value determining whether the sputtering process was the metal or oxide mode. In addition, depending on the sputtering mode, Fe_3O_4 and γ–Fe_2O_3 films can be selectively grown; in other words, the ratios of Fe^{2+} and Fe^{3+} ions are controlled by ϕ_{O_2}. Similar to the case of $Fe_{3-\delta}O_4$ films, the valences of both Fe and Co ions in the $Co_xFe_{3-x}O_4$ films may possibly undergo changes via variation of ϕ_{O_2}, resulting in the observed M_S values of $Co_xFe_{3-x}O_4$ films.

Finally, we briefly comment on the relation between M_S and x. As shown above, M_S equals the saturation magnetization value of bulk $Co_xFe_{3-x}O_4$ for $x = 0.5$ and 0.75 upon carefully tuning the ϕ_{O_2}. Although experimental results for $Co_xFe_{3-x}O_4$ films with $x = 1$ are not presented in this paper, it appears fairly difficult to prepare a $CoFe_2O_4$ film with an M_S comparable with that of the bulk material in our attempts. Assuming that the valencies of Fe and Co are 3+ and 2+, respectively, for the sample corresponding to $x = 1$ and that the film also possesses an inverse spinel structure, the possible combinations of the B-site occupation by the same number of Fe^{3+} and Co^{2+} ions is limited, in the same manner as Anderson's criterion for Verwey ordering in Fe_3O_4.[19] Therefore, it could be difficult for the Fe^{3+} and Co^{2+} ions to migrate between the B-sites and occupy optimized positions within a limited interval of time. As a result the samples with $x \approx 1$ possibly contain a large number of various defects. Although this is no more than a speculation, in order to grow the $Co_xFe_{3-x}O_4$ films with $x = 1$ by the sputtering technique, we speculate that tuning of the other parameters pertaining to the growth conditions may be required.

IV. SUMMARY

We investigated the dependencies of both the magnetization characteristics and the perpendicular magnetic anisotropy of $Co_xFe_{3-x}O_4$ (001) epitaxial films ($x = 0.5$ and 0.75) on the O_2 flow rate in the reactive magnetron sputtering process. The thickness-dependent magnetization measurements revealed the existence of dead-layer regions in the initial stage of the film growth for all films. Our results suggest that the magnetic properties of $Co_xFe_{3-x}O_4$ epitaxial films are governed by the oxidation state and the film structure during initial growth.

ACKNOWLEDGMENTS

This work was supported by the Elements Science and Technology Project of MEXT, Japan. The *MH*-loop measurements were carried out at NIMS, Tsukuba.

[1]S. Chikazumi, *Physics of Ferromagnetism* (Wiley, 1964).
[2]R. Bozorth, E. Tilden, and A. Williams, Phys. Rev. **99**, 1788 (1955).
[3]A. Lisfi, C. M. Williams, L. T. Nguyen, J. C. Lodder, A. Coleman, H. Corcoran, A. Johnson, P. Chang, A. Kumar, and W. Morgan, Phys. Rev. B **76**, 54405 (2007).
[4]J. Inoue, H. Itoh, M. A. Tanaka, K. Mibu, T. Niizeki, H. Yanagihara, and E. Kita, IEEE Trans. Magn. **49**, 3269 (2013).
[5]J. A. Moyer, C. A. F. Vaz, D. P. Kumah, D. A. Arena, and V. E. Henrich, Phys. Rev. B **86**, 174404 (2012).
[6]K. Yosida and M. Tachiki, Prog. Theor. Phys. **17**, 331 (1957).
[7]J. Slonczewski, Phys. Rev. **110**, 1341 (1958).
[8]J. C. Slonczewski, J. Appl. Phys. **32**, S253 (1961).
[9]P. C. Dorsey, P. Lubitz, D. B. Chrisey, and J. S. Horwitz, J. Appl. Phys. **79**, 6338 (1996).
[10]S. Chambers, R. Farrow, S. Maat, M. Toney, L. Folks, J. Catalano, T. Trainor, and G. Brown, J. Magn. Magn. Mater. **246**, 124 (2002).
[11]A. V. Ramos, S. Matzen, J.-B. Moussy, F. Ott, and M. Viret, Phys. Rev. B **79**, 14401 (2009).
[12]W. Huang, J. Zhu, H. Z. Zeng, X. H. Wei, Y. Zhang, and Y. R. Li, Appl. Phys. Lett. **89**, 262506 (2006).
[13]Y. Suzuki, R. B. van Dover, E. M. Gyorgy, J. M. Phillips, V. Korenivski, D. J. Werder, C. H. Chen, R. J. Cava, J. J. Krajewski, J. W. F. Peck, and K. B. Do, Appl. Phys. Lett. **68**, 714 (1996).
[14]H. Yanagihara, K. Uwabo, M. Minagawa, E. Kita, and N. Hirota, J. Appl. Phys. **109**, 07C122 (2011).
[15]C. Jin, H. Liu, P. Li, D. F. Kuang, and H. L. Bai, J. Appl. Phys. **110**, 013917 (2011).
[16]T. Niizeki, Y. Utsumi, R. Aoyama, H. Yanagihara, J.-i. Inoue, Y. Yamasaki, H. Nakao, K. Koike, and E. Kita, Appl. Phys. Lett. **103**, 162407 (2013).
[17]H. Yanagihara, M. Myoka, D. Isaka, T. Niizeki, K. Mibu, and E. Kita, J. Phys. D: Appl. Phys. **46**, 175004 (2013).
[18]D. Margulies, F. Parker, M. Rudee, F. Spada, J. Chapman, P. Aitchison, and A. Berkowitz, Phys. Rev. Lett. **79**, 5162 (1997).
[19]P. W. Anderson, Phys. Rev. **102**, 1008 (1956).