Perpendicular magnetic anisotropy in $CoFe_2O_4$(001) films epitaxially grown on MgO(001)

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We report on the magnetic properties of epitaxial cobalt-ferrite films with orientations parallel to [001] and [111] grown by a reactive molecular beam epitaxy method using pure ozone gas as an oxidation agent. Both Mössbauer spectroscopy and magnetization measurement of the $CoFe_2O_4$(001) film grown on MgO(001) indicate that the film has perpendicular magnetic anisotropy (PMA) with high coercivity, whereas the film of $CoFe_2O_4$(111) grown on α-Al_2O_3(0001) appears to be paramagnetic. The maximum uniaxial anisotropy energy for $CoFe_2O_4$(001) estimated from the magnetization and coercivity at room temperature is $\approx 3 \times 10^6$ erg/cm^3. © *2011 American Institute of Physics*. [doi:10.1063/1.3566079]

The importance of magnetic materials with strong magnetic anisotropy is increasing in the fields of magnetic recording technology and spintronics. The magnetic anisotropy is generally attributed to some symmetry reductions in either local or entire systems. Among the various magnetic materials, typical hard-magnetic compounds are composed of elements with a large spin-orbit coupling, such as noble and/or rare-earth metals, and are utilized for magnetic recording media.[1] Moreover, some ferrites without these heavy elements also show large magnetic anisotropy constants. As the orbital moment of Co^{2+} occupied at B-sites of the spinel structure is relatively large, the magnetocrystalline anisotropy is not negligible even though the crystal structure of $CoFe_2O_4$ is face-centered cubic.[2]

The symmetry reductions induced in the crystals are a necessary condition for perpendicular magnetic anisotropy (PMA). In a thin film, such an emergence of PMA can be introduced by a lattice distortion due to the lattice mismatch between the substrate and the film and/or by the interface between the film and the substrate. There are several reports concerning the magnetic properties of $CoFe_2O_4$ epitaxial films.[3–8] Various magnetic parameters of $Co_xFe_{3-x}O_4$ films, such as the magnetization, the magnetic easy direction, the anisotropy constant, and so forth, appear to be depend on the growth conditions, such as the thickness, the growth temperature, the ratio between Co and Fe, the substrate, growth orientations, and so forth.

In this study, we report on the magnetic properties of epitaxial Co ferrite thin films grown by reactive MBE. We measured the full hysteresis loops of the film at room temperature. The films grown on MgO(001) show strong uniaxial magnetic anisotropy normal to the film surface. The estimated uniaxial magnetic anisotropy constant is $\approx 3 \times 10^6$ erg/cm^3. The origins of the uniaxial anisotropy and the magnetization processes will be discussed.

All the samples were grown using a reactive molecular beam epitaxy system with a pure-ozone generator.[9] Prior to the film growth, cleaved MgO(001) and polished α-Al_2O_3 C-cut substrates with a atomically flat surface were annealed at 700 °C for 1 h. The growth temperature of the $CoFe_2O_4$ films was 220 °C and the growth rate was kept at ≈0.06 Å/s. Depending on the nominal composition, the evaporation rates for both cobalt and iron sources were controlled by an Inficon IC/5 deposition controller. Both metal cobalt and iron sources were evaporated from two independent *e*-guns and the flux rates were monitored using the quartz oscillators. To prepare $CoFe_2O_4$ films for a Mössbauer experiment, we used pure iron with an isotope ratio of ~50% from an ^{57}Fe-enriched source instead of a pure iron source of natural abundance. The conversion electron Mössbauer spectroscopy (CEMS) experiment was performed at room temperature using a He 1% $(CH_3)_3CH$ gas flow counter. The growth rate, total thickness, and surface structures of the $CoFe_2O_4$ films were determined by both x-ray reflectivity measurement and reflection high-energy electron diffraction (RHEED) observations.

Magnetization measurements at room temperature were carried out using a vibrating sample magnetometer (VSM) (Oxford Instruments) equipped with a 12 T magnet. The negative susceptibilities of the diamagnetic substrates and the sample holders were small; however, the applied field exceeded 10 kOe, indicating that the induced moment opposite to the external field was not negligible because the volume of diamagnetic materials are much greater than that of the oxide film. Therefore, the raw data of the magnetization curve appeared to be only diamagnetic at a glance. To extract the ferromagnetic signal from the raw *MH* data, we estimated the diamagnetic susceptibility from the slope of the *MH* curve in the high-field region, where the ferromagnetic component is considered to be saturated, and then the diamagnetic component was subtracted from the raw *MH* hysteresis curve.

Figure 1 shows RHEED patterns of both $CoFe_2O_4$(001) and (111). The RHEED images of the films for both orientations are, respectively, typical patterns for those of the (001)

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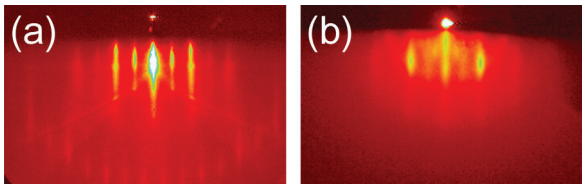

FIG. 1. (Color online) RHEED images of $CoFe_2O_4$ epitaxial films with thickness of 130 Å. (a) $CoFe_2O_4$(001) grown on MgO(001) and (b) $CoFe_2O_4$(111) grown on α-Al_2O_3 (0001).

and (111) surfaces of spinel ferrites. Clear RHEED oscillations only for $CoFe_2O_4$(001) films were observed up to ≈100 Å, indicating that sequential layer-by-layer growth continued at least up to this thickness (Fig. 2). The oscillation period corresponds to a quarter of the lattice constant of $CoFe_2O_4$, similar to those of magnetite[10] and maghemite.[11]

The clear and sharp RHEED pattern as shown in Fig. 1(b) suggests that the film is epitaxial and highly crystalline. While the fact that no RHEED oscillation was observed for the $CoFe_2O_4$(111) film indicates that the growth mode of $CoFe_2O_4$(111) on α-Al_2O_3(0001) films is different from that of $CoFe_2O_4$(001) on MgO(001).

Figure 3 shows the CEMS spectra of the $CoFe_2O_4$(001) and $CoFe_2O_4$(111) epitaxial films with a thickness of ≈130 Å. The sextet spectrum of the film grown on MgO(001) indicates a significant internal field; therefore, the film must be magnetically ordered at room temperature. On the other hand, the broad sextet spectrum of the film grown on α-Al_2O_3(0001) implies a thermally fluctuating magnetic order near the critical temperature or the blocking temperature if it is superparamagnetic.

It is obvious that lines 2–5 of the spectra are weaker than the other lines in the sextets. Ideally, the relative intensity of the six lines in the sextets is $3 : x : 1 : 1 : x : 3$. Here, $x = 4\sin^2\theta/(1+\cos^2\theta)$, and θ is the angle between the hyperfine field (H_{hf}) on the ^{57}Fe nuclei and the incident γ-rays.[10,12] Therefore if x is zero, the moments align to either parallel or antiparallel to the γ-rays. Similarly, if $x = 4$, the moments lie in-plane. In this case, x was measured as $x \approx 0.53$, which corresponds to $\theta \approx 29°$ if all the moments

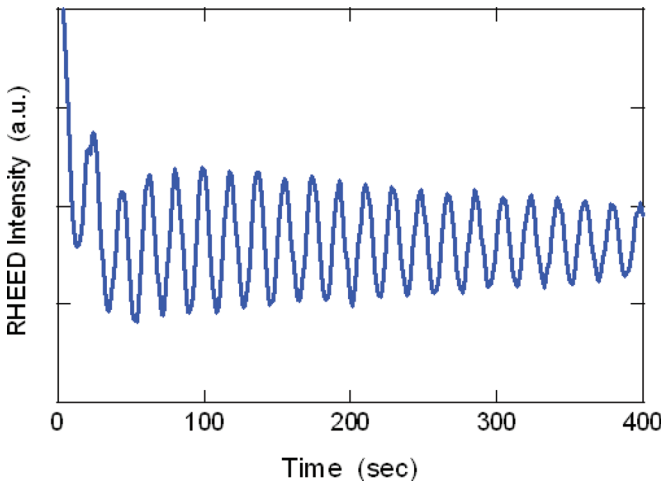

FIG. 2. (Color online) Growth time dependence of specular spot intensity in RHEED images of $CoFe_2O_4$(001) epitaxial film.

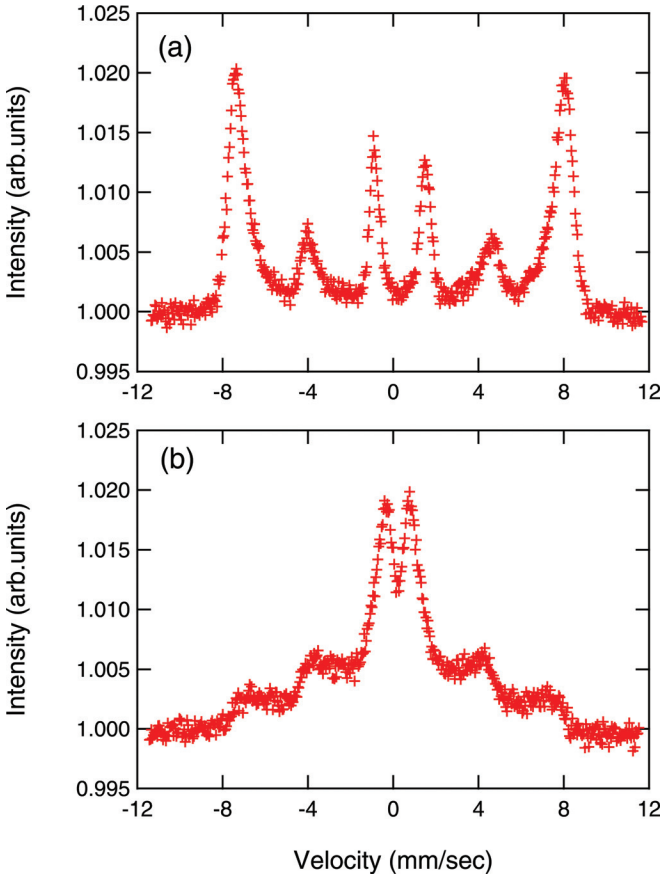

FIG. 3. (Color online) CEMS spectra of (a) $CoFe_2O_4$(001) and (b) $CoFe_2O_4$(111) epitaxial films at room temperature.

align in the same direction without any complicated magnetic domain structure.[13] However, it is difficult to understand why θ was neither 0 nor 90° but slightly tilted from the normal to the film at this moment. This "tilted moments" indicate whether some circular-domain structure with the significant volume of in-plane moments emerged at the remanent state or the preferential direction is 29°-off from the [001]-direction.

The *MH* curve of $CoFe_2O_4$(001) at room temperature is shown in Fig. 4. Similarly to the previous reports on $CoFe_2O_4$ films,[4,8,14,15] the saturation magnetization (M_s) of our $CoFe_2O_4$(001) film of 250 emu/cm^3 is smaller than that of bulk $CoFe_2O_4$.[2] Since there is no sign of an existence of unexpected oxide phases in the RHEED images or x-ray diffraction patterns of the $CoFe_2O_4$(001), the observed significantly smaller M_s could be attributed to the nature of the films. An antiphase boundary (APB) in the spinel ferrite films is the most plausible origin. There also may exist an antisite defect between Co^{2+} at the B-site and Fe^{3+} at the A-site. However the defect cannot explain the moment reduction by itself because the site-change of Co^{2+} at the A-site and Fe^{3+} at the B-site increases the spin number difference between at the A-site and at the B-site, resulting in the increase of the total moment. When an external field was applied parallel to the plane, no hysteresis was observed, meaning that the magnetic easy axis of this film is perpendicular to the film plane. Although the magnetization in the first quadrant is constant, it drops immediately just above the

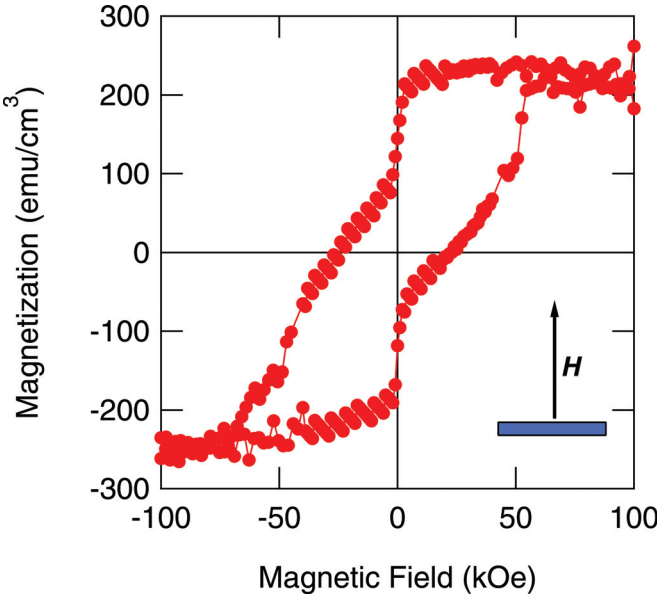

FIG. 4. (Color online) The *MH* curve of $CoFe_2O_4$ (001) epitaxial film with thickness of 130 Å. An external field was applied perpendicular to the film plane.

zero field where the nucleation occurs; therefore, the squareness (the ratio of remanence to saturation moment) is as large as 0.6, which is obviously less than unity. While the CEMS analysis cannot determine whether the average moment of ^{57}Fe ions is parallel to the incident γ-rays or that is antiparallel to the γ-rays. The small squareness suggests that the existence of stripe domains either with some in-plane components or the simply tilted easy directions from the normal to the plane at the remanent state. In the second and third quadrants, the magnetization varies constantly to the negative saturation. Although the *MH* loop is a superposition of two (or more) different *MH* loops at a glance, we could not find any sign of the second phase of Co-/Fe-oxides as mentioned above. Therefore, the observed *MH* should be concluded as the *MH* of the single phase. The positive nucleation field has often been observed in *perfect* single-crystalline PMA films when there are fewer defects that act as retarders of the domain wall motion.[16–18] The observed *MH* loop with low nucleation field suggests that the $CoFe_2O_4$(001) film is of fair quality so that the nucleation easily occurs.

Note that the coercivity (H_c) of the *MH* loop is ≈ 23 kOe. Within the framework of the coherent rotation model,[2] we can roughly estimate the uniaxial anisotropy energy as $K_u = \frac{1}{2}M_sH_c \approx 3 \times 10^6$ erg/cm^3. However, this PMA energy may be an underestimated value, because we considered neither the nucleation process nor the dipole effect attributed to the complicated stripe domain structure. This large K_u is probably due to the lattice misfit between the $CoFe_2O_4$(001) film and the MgO(001) substrate with a tensile stress coupled with a large magnetoelastic coefficient of $CoFe_2O_4$ (Refs. 7, 14, 19). To experimentally obtain a more precise K_u for a more quantitative discussion, magnetic torque measurement is required.

We have succeeded in growing both $CoFe_2O_4$(001) and $CoFe_2O_4$(111) epitaxial films, respectively on MgO(001) and on α-Al_2O_3(0001). The CEMS spectrum of the $CoFe_2O_4$ (001) film indicates that the film is a ferromagnetic (ferrimagnetic) film with PMA. The averaged magnetization orientation in the remanent state was $\approx 29^\circ$ off normal to the film plane. On the other hand, the spectrum of $CoFe_2O_4$(111) suggests that the magnetization fluctuates at room temperature and the magnetic order is either in paramagnetic or superparamagnetic at room temperature. The roughly estimated PMA energy K_u was approximately 3×10^6 erg/cm^3. Although the origin of this large K_u is qualitatively understood as being due to both the large magnetoelastic constant of $CoFe_2O_4$ and the tensile stress between the $CoFe_2O_4$(001) film and the MgO (001) substrate, the magnetic properties of the film are not yet understood from the microscopic point of view.

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[13] In our CEMS setup, the distance between the γ-ray source and the film is approximately 5 cm and the sample size is 1×1 cm^2. For this geometry, the in-plane component of CEMS is negligibly small. The estimated intensity of the 2–5 lines is about a hundredth of that of the 3–4 lines even if all the moments point perfectly out-of-plane.
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