Reduced magnetocrystalline anisotropy of CoFe$_2$O$_4$ thin films studied by angle-dependent x-ray magnetic circular dichroism

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Spinel-type CoFe$_2$O$_4$ is a ferrimagnetic insulator with the Néel temperature exceeding 790 K, and shows a strong cubic magnetocrystalline anisotropy (MCA) in bulk materials. However, when a CoFe$_2$O$_4$ film is grown on other materials, its magnetic properties are degraded so that so-called magnetically dead layers are expected to be formed in the interfacial region. We investigate how the magnetic anisotropy of CoFe$_2$O$_4$ is modified at the interface of CoFe$_2$O$_4$/Al$_2$O$_3$ bilayers grown on Si(111) using x-ray magnetic circular dichroism (XMCD). We find that the thinner CoFe$_2$O$_4$ films have significantly smaller MCA values than bulk materials. The reduction of MCA is explained by the reduced number of Co$^{2+}$ ions at the $O_h$ site reported by a previous study [Y. K. Wakabayashi et al., Phys. Rev. B 96, 104410 (2017)].

INTRODUCTION

Spinel-type cobalt ferrite CoFe$_2$O$_4$ is a classical ferrimagnetic insulator having the Néel temperature exceeding 790 K and exhibits a strong cubic magnetocrystalline anisotropy (MCA). The cubic MCA has been successfully explained by the single-ion anisotropy of the Co$^{2+}$ ions at the inequivalent $O_h$ sites [1]. Recently, heterostructures incorporating thin CoFe$_2$O$_4$ layers have attracted much attention as spintronics devices [2] because of the spin-dependent band gap [3] and high Néel temperature of CoFe$_2$O$_4$ [4]. For example, a CoFe$_2$O$_4$-based tunnel barrier acts as a spin filter because electrons have spin-dependent tunneling probabilities [5]. However, the experimentally obtained spin-filtering efficiency of CoFe$_2$O$_4$-based tunnel barriers still remains lower than theoretical values of 100% [2, 6, 7]. As a possible cause of the low spin-filtering efficiency, it has been proposed that structural and/or chemical disorder lead to the formation of impurity states in the spin-dependent gap [3, 8, 9]. In order to improve the spin filtering efficiency, it is thus essential to understand the electronic and magnetic phenomena at the interfaces.

In a recent work [10], the magnetic properties of CoFe$_2$O$_4$(111)/Al$_2$O$_3$(111)/Si(111) structures [11] were studied using the element-specific probe of x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD). A schematic illustration of the stacking structure of the sample and an example of cross sectional transmission-electron-microscope (TEM) image are shown in Fig. 1(a). Because they employed the total-electron yield (TEY) method to detect the absorption signals, several nanometers from the surface were preferentially probed [12, 13]. By reducing the film thicknesses below the probing depth of a few nm, they obtained XAS and XMCD spectra reflecting the magnetically dead layers of ∼1.4 nm thickness and the cation redistribution near the CoFe$_2$O$_4$/Al$_2$O$_3$ interface as illustrated in Fig. 1(b). They revealed a high density of Co-Fe antisite defects and the reduced concentration of the Co$^{2+}$ ions at the $O_h$ sites reported by a previous study [Y. K. Wakabayashi et al., Phys. Rev. B 96, 104410 (2017)].
EXPERIMENTAL METHODS

Epitaxial CoFe$_2$O$_4$(111) thin films with the thicknesses of $d = 1.4$, 2.3, 4, and 11 nm were grown on a 2.4 nm-thick $\gamma$-Al$_2$O$_3$(111) buffer layer/n$^+$-Si(111) substrate using the pulsed laser deposition method. In order to avoid charging of the samples during the XAS and XMCD measurements, we used heavily phosphorus-doped Si(111) wafers with low resistivities of 2 m$\Omega$ cm. For the epitaxial growth of the $\gamma$-Al$_2$O$_3$ buffer layers on the Si substrates, we used solid-phase reaction of Al and SiO$_2$. A more detailed description of the sample preparation and characterization is given in Ref. [10].

Magnetic field-angle-dependent XAS and XMCD measurements were performed at room temperature using a superconducting vector-magnet XMCD apparatus [16] installed at the undulator beamline BL-16A of Photon Factory, High Energy Accelerator Research Organization (KEK-PF). The magnetization $M$ of CoFe$_2$O$_4$ thin film is rotated by the magnetic field $H$. The magnetic field angle $\theta_H$ and magnetization angle $\theta_M$ are defined relative to the surface normal. The absorption signals were detected in the TEY mode. The XMCD signals were collected by switching the photon helicity at the rate of 10 Hz [17]. In order to eliminate the saturation effect [18], which induces an extrinsic angle dependence to spectral line shapes, we fixed the x-ray incident angle at 45° and applied magnetic fields of 0.7 T to the sample along various directions. The geometry of the present measurements is illustrated in Fig. 2(a).

RESULTS AND DISCUSSION

Figures 2(b) and (c) show the Fe $L_{2,3}$-edge XAS ($\mu^+ + \mu^-$) and XMCD ($\mu^+ - \mu^-$) spectra of the 11 nm-thick CoFe$_2$O$_4$ thin film. Here, $\mu^+$ ($\mu^-$) denotes the absorption coefficient for photons with positive (negative) helicity. Since the spectral line shape of XAS did not show any appreciable $\theta_H$ dependence, only the spectrum at $\theta_H = 0°$ is shown. Figure 2(c) shows that the XMCD spectrum systematically changes with $\theta_H$. Since the XMCD intensity is proportional to the magnetic moment projected onto the x-ray incident direction ($M_{\text{proj}} = M \cos(\theta_M - 45°)$), its $\theta_H$ dependence reflects the change of the magnetization direction $\theta_M$ under varying $\theta_H$. Since the total magnetic moment and the Fe $L_{2,3}$-edge XMCD spectra of these samples were already obtained in Ref. [10], we deduced $M_{\text{proj}}$ from the
intensity of Fe $L_{2,3}$-edge XMCD under the assumption that the Fe $L_{2,3}$-edge XMCD intensity is proportional to $M$. Figure 2(d) shows the $\theta_H$ dependence of $M_{\text{proj}}$. If this film has neither magnetocrystalline nor magnetic shape anisotropy, $M$ would be fully aligned to the magnetic field direction ($\theta_H = \theta_M$) and thus $M_{\text{proj}}$ should be $M \cos(\theta_H - 45^{\circ})$, as shown by a gray dashed curve. The deviation of the experimental data from $M \cos(\theta_H - 45^{\circ})$ thus shows the magnetic anisotropy.

In order to analyze the obtained $\theta_H$ dependence of $M_{\text{proj}}$, we use the Stoner-Wohlfarth model [14, 19]. According to the model, the magnetic energy density $E$ of a thin film is given by:

$$E = -\mu_0 M H \cos(\theta_M - \theta_H) + \frac{\mu_0}{2} M^2 \cos^2 \theta_M + E_{\text{MCA}},$$

where $\mu_0$ is the vacuum permeability, and the other variables are defined in Fig. 2(a). In Eq. (1), $E$ is the sum of the Zeeman energy [$-\mu_0 M H \cos(\theta_M - \theta_H)$] and the magnetic anisotropy energy. The magnetic anisotropy energy consists of two contributions. One is the shape anisotropy (SA) energy, which originates from the demagnetizing field of the film, and the other is the MCA energy, which has a microscopic origin. Note that the Stoner-Wohlfarth model is applicable not only to the ferromagnetic state but also to the paramagnetic state if the Co$^{2+}$ (O$_{h}$) is expected to have dominant effects on the MCA. Such modifications of magnetic anisotropy induced by the distribution of Co$^{2+}$ (O$_{h}$) are also reported for the CoFe$_2$O$_4$ nanoparticles [21–23]. The cation distribution in these films has been studied using XMCD by Wakabayashi et al. [10], according to which the inversion parameter $y$, defined by the chemical formula [Co$_{1-y}$Fe$_y$]$_3$[Fe$_{2-y}$Co$_y$]O$_3$O$_4$, suddenly decreases in the $d \leq 2.3$ nm region as shown in Fig. 3(f). From the comparison of $y$ and the normalized MCA (the magnitude of MCA divided by $M$) as functions of the film thickness $d$ plotted in Fig. 3(f), one can see that the reduction of MCA with decreasing film thickness qualitatively follows the reduction of $y$. This result implies that the reduction of the normalized MCA originates from the reduction of the Co$^{2+}$ (O$_{h}$) ions in the interfacial region.

**CONCLUSION**

We have investigated the magnetic anisotropy of the epitaxial CoFe$_2$O$_4$(111) thin films (thicknesses $d =$11, 4, 2.3, and 1.4 nm) grown on the 2.4 nm-thick $\gamma$-Al$_2$O$_3$(111) buffer layer/n$^{+}$-Si(111) substrates using magnetic field-angle-dependent XAS and XMCD. We have found that the MCA of the interfacial region including the magnetically dead layer is reduced. We attribute the reduction of MCA to the thickness-dependent cation redistribution in the interfacial region, that is, to the abrupt reduction of the Co$^{2+}$ (O$_{h}$)-ion concentration in the interfacial region.

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FIG. 3. Experimental and calculated $M_{\text{proj}}$ of CoFe$_2$O$_4$ thin films. (a)–(d) Experimentally obtained $M_{\text{proj}}$ and calculations for the films with various thicknesses ($d = 11$, $4$, $2.3$, and $1.4$ nm). (e) Difference curves between the experimental and calculated $M_{\text{proj}}$ in panels (a)–(d). Note that the vertical scale gradually changes from (a) to (d). (f) Comparison between the difference curves shown in panels (a)–(d) and the inversion parameter $y$ reported in Ref. [10]. Note that the difference curves [shaded area in panel (e)] have been divided by the magnetization $M$ in each film.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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