Structural, Magnetic, and Electric Properties of Pt/Co/Au/Cr₂O₃/Pt Thin Film with Cr₂O₃ Layer below 25 nm

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Perpendicular exchange bias using magnetoelectric Cr₂O₃ has an electric-field triggered switching ability, and the thickness limit of the Cr₂O₃ layer for inducing this bias is a topic of research. In this paper, we investigated the structural, magnetic, and electric properties of Pt/Co/Au/Cr₂O₃/Pt thin films with a Cr₂O₃ layer in the thickness range of 5.7 to 25 nm. By using a magnetron sputtering method, a well-crystallized Cr₂O₃(0001) layer was formed in 5.7-nm-thick Cr₂O₃. All studied films showed perpendicular magnetic anisotropy. The uniaxial magnetic anisotropy energy density increased as the Cr₂O₃ thickness decreased, and 810±90 kJ/m³ was obtained for the film with 5.7-nm-thick Cr₂O₃. Perpendicular exchange bias was evaluated above 80 K, and an exchange anisotropy energy density of 0.30 mJ/m² was observed for the film with a 25-nm-thick Cr₂O₃ at 80 K. The exchange bias could not be observed below 18 nm. Instead, coercivity enhancement, which yields the exchange bias by precisely controlling interfacial exchange coupling, was observed. The electric resistivity was about $5 \times 10^5 \Omega \cdot \text{m}$ for the 5.7-nm-thick Cr₂O₃ layer, which is sufficiently high for magnetoelectric applications.

Keywords: Cr₂O₃, antiferromagnet, thin film, perpendicular magnetic anisotropy, insulator

1. Introduction

Future memory/logic devices beyond CMOS require several severe working conditions such as low-energy operation below 10 atto-J (aJ) and fast switching below 1 ns¹⁾. The magnetoelectric (ME) effect, which results from coupling between magnetic and electric fields, can be a solution for creating low energy input methods for these devices. The ME effect is recognized as the effect of spontaneous magnetization (M) induction by an electric field (E) or electric polarization (P) induction by a magnetic field (H)^{2,3)}. The strength of the ME effect is characterized by using ME susceptibility as follows.

$$\alpha_{ij} = dM_i/dE_j = dP_j/dH_i \quad (1)$$

The ME effect is sometimes observed in antiferromagnetic (AFM) insulators where α_{ij} is coupled with an AFM order parameter⁴⁾. Eventually, the sign of α_{ij} is reversed and accompanied with the reversal of the Néel vector. The driving force of the reversal is expressed by⁴⁾

$$2\alpha_{ji}E_iH_j, \quad (2)$$

which is reminiscent of the Zeeman energy of ferromagnetic (FM) materials in that the spontaneous magnetization of the FM layer is replaced with the E -induced magnetization $\alpha_{ji}E_i$.

Cr₂O₃ is a well-known ME-AFM insulator, and the above-mentioned reversal of α_{ij} was first detected by directly measuring α_{ij} for bulk Cr₂O₃⁴⁾. Although Cr₂O₃ is a proto-typical ME-AFM material, it has advantages compared with other single-phase multiferroic materials, such as simple preparation based on a conventional

sputtering technique and a sole cation species that can prevent the crystalline quality from being deteriorated by the incorrect site occupation of other cations. Despite these advantages, the application of the ME effect in Cr₂O₃ has been regarded as difficult because the ME effect for Cr₂O₃ is a linear effect; the ferroic feature vanishes by removing E or H ^{2,3,5)}. In 2005, Borisov *et al.* complemented the linear ME effect by using an exchange bias⁶⁾. In this scheme, the interfacial AFM spin/domain state, which is coupled with an AFM order parameter (the Néel vector), is detected by exchange bias polarity. When the AFM spin/domain state (the Néel vector) is reversed by the ME effect, this reversal is accompanied with a change in the exchange bias polarity. In particular, when the exchange bias field is higher than the coercivity, the magnetization direction of the FM layer after the field is removed reverses definitely. This scheme has been experimentally proven using the FM/Cr₂O₃(0001) thin film system^{7,8)}.

The above device scheme is designed upon the prerequisite that the film has a perpendicular exchange bias higher than the coercivity, and hence, the lowest Cr₂O₃ thickness at which perpendicular exchange bias can be induced would determine the low thickness limit of the device. According to the magnetic domain wall (DW) model^{9,10)}, the critical AFM layer thickness for inducing exchange bias is relevant to the DW width of the AFM layer along the film thickness direction. For the case of Cr₂O₃(0001) thin film, the DW width along the c -axis was calculated in the range of 20-70 nm depending on the lattice parameter¹¹⁾. Recently, ME-induced switching of the perpendicular exchange bias was demonstrated using 30-nm-thick Cr₂O₃(0001) thin film¹²⁾, and perpendicular exchange bias using a Cr₂O₃(0001)

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layer was confirmed for film with 20-nm-thick Cr_2O_3 ¹³⁾; for both cases, the Cr_2O_3 thickness was near the DW width. In this paper, we explored the possibility of the perpendicular exchange bias persisting below the 20-nm-thick $\text{Cr}_2\text{O}_3(0001)$ layer as well as the electric properties that are also important for electric field application.

2. Experimental methods

The stacking structure of the fabricated sample was a Pt(2 nm)/Co(0.5 nm)/Au(0.5 nm)/ $\text{Cr}_2\text{O}_3(t_{\text{Cr}_2\text{O}_3} = 5.7, 12, 18, 25 \text{ nm})$ /Pt(20 nm)/ $\alpha\text{-Al}_2\text{O}_3(0001)$ substrate. The thicknesses of the Co and Au layer were in a few monolayer regime, and these were the nominal thicknesses. The Au space layer was used to tune the interfacial exchange coupling strength between the Co and Cr_2O_3 so that the coercivity enhancement could be suppressed when the exchange bias was manifested¹⁴⁾. The substrate was ultrasonically cleaned using acetone, ethanol, pure water, and isopropanol. Each layer was deposited by using a DC magnetron sputtering method. The Pt, Co, and Au layers were deposited using pure Ar, and the Cr_2O_3 layer was deposited by using a reactive sputtering method with a gas mixture of Ar and O_2 . Before the deposition, the substrate was degassed at 873 K and, subsequently, the Pt buffer layer was deposited at 873 K. The deposition temperature of the Cr_2O_3 layer was 773 K. The Pt capping layer, Co, and Au layers were deposited at room temperature.

Structural characterizations were carried out using reflection high-energy electron diffraction (RHEED), X-ray reflectometry (XRR), and high-angle X-ray diffraction (XRD). For the RHEED observations, the sample was once cooled down to room temperature after the deposition and transferred to a RHEED chamber that was directly connected to the deposition chamber through an ultra-high vacuum gate valve. The XRR and XRD measurements were carried out using Cu $K\alpha$ irradiation with a Ge (220) $\times 2$ monochromator.

Magnetic properties were characterized on the basis of magnetization curves measured using a vibrating-sample magnetometer (VSM) and magneto-optic Kerr effect (MOKE) measurements. The VSM measurements were done at room temperature ($\sim 300 \text{ K}$) for the applied magnetic field direction parallel and perpendicular to the film plane. MOKE loops were measured with a polar configuration where the incident angle of light ($\lambda = 670 \text{ nm}$) was 10° from the surface normal. The MOKE measurements were carried out in a temperature regime from 80 K to 300 K.

3. Results and discussions

3.1 Structural characterizations

Figure 1 shows RHEED images of the 5.7-nm-thick Cr_2O_3 layer, which was the lowest case in this paper. For both electron azimuths, equally spaced streaks were observed, which indicate the flat surface and aligned

Fig. 1 RHEED images for 5.7-nm-thick Cr_2O_3 layer. Electron azimuth was (a) $[11\bar{2}0]$ and (b) $[1100]$ of $\alpha\text{-Al}_2\text{O}_3(0001)$ substrate.

Fig. 2 (a) High-angle XRD profiles and (b) XRR profiles for films with different $t_{\text{Cr}_2\text{O}_3}$. * in (a) represents diffraction from substrate. Dotted gray line shows guide line for diffraction peak position of Pt(111) and Pt(222) calculated using bulk lattice parameter.

Fig. 3 (a) Magnetization curves for film with $t_{\text{Cr}_2\text{O}_3} = 5.7$ nm. Red and blue curves represent curves for applied magnetic field direction perpendicular and parallel to film plane, respectively. (b) Change in $K_{\text{U_eff}}$ with $t_{\text{Cr}_2\text{O}_3}$ evaluated from magnetization curves.

crystallographic orientation in the growth direction. The diffraction patterns can be explained by the corundum (0001). In addition, the symmetric pattern in the [1120]-azimuthal RHEED pattern indicates twin formation with a twin boundary along [1120]. Similar RHEED patterns were observed for every $t_{\text{Cr}_2\text{O}_3}$. In our previous reports¹⁴, the Au layer grown on the $\text{Cr}_2\text{O}_3(0001)$ layer was polycrystalline, and the subsequent Co and Pt layer showed a weak (111) orientation. We confirmed a similar structure for the films studied in this paper. Figure 2(a) shows high-angle XRD profiles wherein the diffraction peaks were near $2\theta = 40^\circ$ and 85° except for the diffractions from the substrate (indicated by *). The former and latter diffraction peaks originated from Pt(111) [or $\text{Cr}_2\text{O}_3(0006)$] and Pt(222) [or $\text{Cr}_2\text{O}_3(00012)$], respectively, which was consistent with the RHEED observations. Because the d -spacings for Pt(111) and $\text{Cr}_2\text{O}_3(000)$ were almost same, it was difficult to distinguish these two in the XRD profiles. Nonetheless, the peak intensity was almost independent of $t_{\text{Cr}_2\text{O}_3}$, and thus, we believe that the diffraction was mainly from the

Fig. 4 (a) Temperature dependence of $\mu_0 H_{\text{EX}}$ and $\mu_0 H_{\text{C}}$ for film with $t_{\text{Cr}_2\text{O}_3} = 25$ nm. (b) Temperature dependence of $\mu_0 H_{\text{C}}$ for films with $t_{\text{Cr}_2\text{O}_3} = 18$ nm (blue), 12 nm (red), and 5.7 nm (black). Magnetization curves for film with $t_{\text{Cr}_2\text{O}_3} = 5.7$ nm. Open gray circles are $\mu_0 H_{\text{C}}$ for reference film, Pt/Co bilayer on $\alpha\text{-Al}_2\text{O}_3(0001)$ substrate.

Pt buffer layer. This should be reasonable because the atomic scattering factor of Pt is higher than those of Cr^{3+} and O^{2-} .

For qualitative discussion on the interfacial magnetic properties shown below, we indirectly evaluated interface roughness on the basis of XRR measurements. Figure 2(b) shows XRR profiles of the fabricated films. The profiles show clear oscillation up to $2\theta = 10^\circ$ except for the film with $t_{\text{Cr}_2\text{O}_3} = 18$ nm, where the oscillation disappeared at about $2\theta = 4^\circ$. The results indicate that films except for that with $t_{\text{Cr}_2\text{O}_3} = 18$ nm had a sharp interface, and that with $t_{\text{Cr}_2\text{O}_3} = 18$ nm was relatively rough. The theoretical fitting implies that the interface roughness at the FM(Pt/Co/Au)/ Cr_2O_3 interface was about 0.3 nm for the former three films and about 0.8 nm for the film with $t_{\text{Cr}_2\text{O}_3} = 18$ nm.

3.2 Magnetic properties

Figure 3 shows magnetization curves (M - H curves) measured at room temperature for the film with $t_{\text{Cr}_2\text{O}_3} = 5.7$ nm. The saturation magnetization was about 1600 kA/m, which was higher than the value for the bulk Co (~ 1400 kA/m) possibly because of the sizable spin

polarization of Pt (and Au)^{15,16}. The M - H curve with H perpendicular to the film plane showed a rectangular hysteresis with the remanence ratio of unity. In contrast, the M - H loop with H parallel to the film plane was almost linear below $\mu_0 H$ at about 1 T, and no clear hysteresis was observed. The results show that the film showed perpendicular magnetic anisotropy. The uniaxial magnetic anisotropy energy density K_{U_eff} was evaluated using

$$K_{U_eff} = \left(\int_0^{M_S} H dM \right)_{H \parallel \text{Film}} - \left(\int_0^{M_S} H dM \right)_{H \perp \text{Film}}, \quad (3)$$

where M_S denotes the saturation magnetization. In Fig. 3(b), the change in K_{U_eff} with $t_{Cr_2O_3}$ is shown. K_{U_eff} is typically within several 100 kJ/m³. The dispersion of the values may be due to the difference in the micro-structure of the Co layer because the Co thickness was in a few monolayer regime. The reduction in K_{U_eff} for the film with $t_{Cr_2O_3} = 18$ nm should be due to the large roughness mentioned above.

Figure 4(a) shows the temperature dependence of the exchange bias field ($\mu_0 H_{EX}$) and the coercivity ($\mu_0 H_C$) for the film with $t_{Cr_2O_3} = 25$ nm measured on the basis of polar MOKE. An exchange bias field of $\mu_0 H_{EX} = 390$ mT was observed at 80 K and increased to 410 mT at 100 K. The increase in $\mu_0 H_{EX}$ as temperature increased is attributed to interfacial Cr^{3+} spin canting¹⁷. The exchange bias abruptly disappeared at 102 K, and the coercivity was enhanced, accompanied with a disappearance of the exchange bias. This abrupt disappearance was observed for the FM/ Cr_2O_3 (0001) stacked film^{13,18} and is likely to be a unique feature of this system. Details on this unique temperature dependence can be found in our previous review¹⁹. Below a $t_{Cr_2O_3}$ of 18 nm, the exchange bias could not be observed above 80 K. In Fig. 4(b), the temperature dependence of $\mu_0 H_C$ for the films with $t_{Cr_2O_3}$ below 18 nm are shown. The $\mu_0 H_C$ (open gray circle) for the Pt/Co bilayer on the α - Al_2O_3 (0001) substrate is also shown as a reference. As in the case of $t_{Cr_2O_3} = 25$ nm above 102 K, the coercivity increased as the temperature decreased. Although a direct comparison of the absolute value of coercivity is difficult because coercivity can be affected by structural defects and micro-structures, it is likely that the $\mu_0 H_C$ values at 300 K were similar for the Pt/Co/Au/ Cr_2O_3 /Pt films and the reference sample (Pt/Co bilayer on the α - Al_2O_3 substrate).

Below 280 K ($\sim$ Néel temperature of Cr_2O_3 thin film²⁰), the coercivity of the Pt/Co/Au/ Cr_2O_3 /Pt films seemed to be enhanced compared with the reference sample, and this enhancement was observed for the film with $t_{Cr_2O_3} = 5.7$ nm.

As previously discussed, the onset temperature of the exchange bias in the FM/ Cr_2O_3 system can be controlled by the spacer layer thickness^{14,21}, i.e., the strength of the interfacial exchange coupling. Hence, when we precisely control the interfacial exchange coupling, it is expected that exchange bias might be achieved for a low $t_{Cr_2O_3}$ below 18 nm. That is, in this work, the Au spacer thickness was fixed at 0.5 nm. If a little thicker, the Au spacer layer would reduce the interfacial exchange coupling, which would yield the perpendicular exchange bias in the high temperature regime. In comparison, a

Fig. 5 (a) Optical microscope image of devices used for electric characterizations. Electric circuit is also drawn. Right image is schematic drawing of cross-section of device. (b) I-V curve and (c) temperature dependence of resistivity for films with $t_{Cr_2O_3} = 12$ (red) and 5.7 (blue) nm.

thicker Au layer would also reduce the exchange bias field. To realize this, very precise control of the Au spacer thickness is necessary; this is future work.

3.3 Electric properties

For electric-field triggered switching including the ME-based mechanism, sufficient resistivity is also essential. In most previous reports on ME-induced switching of the perpendicular exchange bias using Cr_2O_3 thin film, thick Cr_2O_3 above 100 nm was often used^{7,8,22}, although, very recently, we reported a scheme using Cr_2O_3 thin film below 50 nm^{12,23}. There are few reports on the insulating properties of the Cr_2O_3 layer in the thickness regime below 30 nm. To investigate the electric properties, the micro-dot with a 30-μm diameter shown in Fig. 5(a) was fabricated by photolithography, Ar ion milling, and a lift-off technique. Using this device, IV curves and the temperature dependence of the resistivity were measured on the basis of a two-terminal method. Figure 5(b) shows an IV curve

measured at 300 K. For both films with $t_{\text{Cr}_2\text{O}_3} = 12$ and 5.7 nm, the FV curves showed a non-linear increase, which indicates that the device had an insulating feature. The asymmetry in the FV curves should be due to the different materials of the top (Pt/Co/Au) and bottom (Pt) electrodes. As shown in Fig. 5(c), the resistivity increased as temperature decreased in an exponential manner, which also supports the insulating feature of the fabricated Cr_2O_3 layer. The resistivity, evaluated by the derivative of the FV curve [Fig. 5(b)], was about $3 \times 10^6 \Omega \cdot \text{m}$ and $5 \times 10^5 \Omega \cdot \text{m}$ for the films with $t_{\text{Cr}_2\text{O}_3} = 12$ and 5.7 nm, respectively. These values are similar to the reported resistivity for 300-nm-thick Cr_2O_3 ²⁴⁾. In addition, the leakage current density at $E = +60$ MV/m was about 300 A/m², which is similar to the case of the 30-nm-thick Cr_2O_3 film where ME-induced switching of the exchange bias was confirmed¹²⁾. That is, the resistivity was sufficiently high enough to apply the scheme to the ME-induced switching of perpendicular exchange bias.

4. Summary

We investigated the structural, magnetic, and electric properties of Pt/Co/Au/ Cr_2O_3 /Pt thin films with a Cr_2O_3 thickness below 25 nm. Well-crystallized Cr_2O_3 thin film could be prepared in a 5.7-nm thickness by using a reactive magnetron sputtering method. The film showed perpendicular magnetic anisotropy at room temperature. The uniaxial magnetic anisotropy energy density is typically on the order of several 100 kJ/m³. Perpendicular exchange bias, evaluated above 80 K, was observed for a film with $t_{\text{Cr}_2\text{O}_3} = 25$ nm. Although below 18 nm, the bias was not observed above 80 K, a comparison with a Pt/Co bilayer on an $\alpha\text{-Al}_2\text{O}_3$ substrate suggested a coercivity enhancement. Hence, the exchange bias is expected to appear through the precise control of the interfacial exchange coupling strength. An insulating feature was maintained for the 5.7-nm-thick Cr_2O_3 layer, and the resistivity was about 5 M $\Omega \cdot \text{m}$, which is comparable to the reported value for thick film above 30 nm and is sufficiently high enough to apply the ME-induced switching device scheme.

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