The effect of electric fields on magnetism has attracted much attention given its importance from a fundamental perspective as well as its potential for use in magnetic storage applications. The change in the Curie temperature $T_C$ upon the application of an electric field was first reported for a ferromagnetic semiconductor. Subsequently, the phenomenon was observed at room temperature in an ultrathin metallic film of Co. Although solid-state capacitor (SSC) structures with magnetic electrodes are used widely, a very large change in $T_C$ of up to 100 K was recently realized using an electric double-layer capacitor (EDLC) structure that employed an ionic liquid. In addition to the modulation of $T_C$, control of the coercivity or magnetic anisotropy (MA) is of great importance from an application viewpoint, because it is expected to decrease the power required for the write operation of magnetic storage devices. The mechanism underlying the effect of electric fields on MA has been generally considered to be the change in the occupancy of electrons in the $d$-orbital caused by a Fermi level shift and/or a change in the electronic state. The screening length of an electric field in metals is generally smaller than one monolayer in thickness. Thus, only the interfacial MA is sensitive to electric fields within this framework. However, it has been suggested that other factors can cause a change in the total MA in both SSC and EDLC structures, such as an oxidation reaction (or oxygen-ion migration). This is a thermally activated effect. Thus, the change in the magnetism is expected to be slow. On the other hand, magnetization switching on the order of nanoseconds has been achieved in SSCs (e.g., magnetic tunnel junctions). Further, in an SSC with a HIO$_3$ gate insulator, the changes in the valence and atomic distance of Co with the application of an electric field were confirmed to be negligibly by means of X-ray reflectometry. Therefore, elucidation of the phenomenon of charge accumulation and related chemical effects is of great importance.

In this study, we identified these mechanisms by using Co thin films deposited on a Pt underlayer through investigation of the Co thickness dependence of the MA under application of an electric field. It was found that the bulk MA and not the interfacial MA was altered after the mild oxidation of the Co layer; this was confirmed from the Co layer thickness dependence of the MA before and after the intentional oxidation. The results obtained were similar to those for the case where a Co anode was used in an EDLC under ionic liquid gating. On the other hand, only the interfacial MA changed when the Co layer was the cathode, suggesting that in this case, charge accumulation was most likely the primary mechanism responsible for the change in the MA.

The Pt/Co layers were deposited on a semi-insulating GaAs(001) substrate or an intrinsic Si(001) substrate by rf sputtering at room temperature. The layer structure from the substrate side was the following: Ta (3.0 nm)/Pt (3.0 nm)/Co ($t_{Co}$/MgO (2.0 nm). The MgO layer was the cap layer and was formed to prevent oxidation of the Co surface upon exposure to air. Several samples with different $t_{Co}$ values (0.48–2.0 nm) were prepared. From X-ray diffraction (XRD) measurements performed using the conventional $\theta$–$2\theta$ method with Cu-Kα radiation [see the solid line in Fig. 1(a)] and transmission electron microscopy observations of the as-deposited samples, it was confirmed that the Pt layer in the samples had an fcc(111)-oriented texture. Further, the MgO layer had an amorphous or polycrystalline texture. A very weak XRD peak was detected at $2\theta$ of 43° [see Fig. 1(a)]; this was probably attributable to the fcc(111) or hcp(0002) plane of the Co layer. The thickness fringe observed in the low 2$\theta$ range (2–8°) (also see the inset) suggested that the top and bottom interfaces of the metallic layers were sharp.

To evaluate the degree of oxidization of the Co layer, X-ray photoelectron spectroscopy (XPS) measurements were performed. Figure 1(b) shows the XPS scans of the Co 2p state at 300 K for two samples with $t_{Co} = 1.0$ nm: the as-deposited sample and the sample subjected to oxygen plasma ashing (OPA). To compare the samples, the as-deposited sample was cut into two pieces, and one of them was subjected to the OPA treatment. The XPS spectra shown in the figure are the averaged results of the data obtained by changing the X-ray incident angle (21.9–78.1°) from the normal to the film plane. The OPA treatment was performed for 30 s at an rf power of 150 W in an oxygen atmosphere at 50 Pa. A clear peak corresponding to the Co–O binding state was observed in the sample subjected to the OPA treatment.
However, no peak was detected at this position in the case of the as-deposited sample, suggesting that the Co layer existed in a purely metallic state. A detailed analysis of the incident angle dependence of the XPS scans revealed that the depth of oxidation after the OPA treatment was less than half the thickness of the Co layer from the surface and that the deeper regions contained pure metallic Co. In addition to the XPS thickness of the Co layer from the surface and that the deeper regions contained pure metallic Co. In addition to the XPS data for sample with \( t_{\text{Co}} = 1.0 \) nm for the two conditions.

In order to further study the effects of an electric field on the MA as well as on the magnetic moments of the fabricated samples, direct magnetization measurements were performed using a superconducting quantum interference device (SQUID) magnetometer. In addition, Hall measurements were performed under a gate voltage \( V_G \). In Hall measurements, the Hall resistance \( R_{\text{Hall}} \) is proportional to the perpendicular component of the magnetization because of the anomalous Hall effect. The as-deposited samples with various \( t_{\text{Co}} \) values were used for the measurements. For the SQUID measurement, the samples were cut into approximately \( 2 \times 5 \) mm\(^2\) pieces. For the Hall measurements, a 1-mm-wide wire with Hall probes was fabricated using photolithography and Ar ion milling. Then, a polymer film of an ionic liquid (i.e., an ionic liquid film) composed of \( N,N,N\)-trimethyl-\( N\)-propylammonium (TPMA\(^+\)) and bis(trifluoromethanesulfonyl)imide (TFSI\(^-\)) with a 50-nm-thick Au top gate electrode was directly put on the sample to form an EDLC structure. The schematic illustration in the inset of Fig. 2 shows the cross-section of the device structure. \( V_G \) was changed at 300 K for all the measurements. The measurements were performed at 200 K, which was lower than the melting point of the ionic liquid used (~290 K\(^{27}\)). Thus, \( V_G \) was removed during each measurement when the temperature \( T \) was reduced to 200 K, because the EDL was fixed at this temperature, regardless of whether or not \( V_G \) was applied. The Co layer was defined as the cathode (anode) side during the application of positive (negative) \( V_G \).

Figure 2 shows the \( R_{\text{Hall}} \) curve obtained by sweeping of the perpendicular magnetic field \( \mu_0 H_\perp \) at various \( V_G \) values for the sample with \( t_{\text{Co}} = 1.0 \) nm. The curve for \( V_G = 0 \) V showed that the sample exhibited in-plane MA, because the perpendicular MA (PMA) energy was lower than the demagnetization energy. When \( V_G \) of +2 V was applied, the saturation field increased, resulting in the weakening of the PMA. On the other hand, application of \( V_G \) of −1 V resulted in an enhancement of the PMA. At \( V_G \) of −2 V, a clear hysteresis loop was observed, indicating that the sample had stronger PMA. The direction of change in the MA was consistent with the results of previous electric field experiments on SSCs [Fe/MgO,\(^{6,10}\) CoFeB/MgO,\(^{6,10}\) or Pt/Co/MgO/HfO\(_2\) (at 200 K\(^{11}\)systems). For the measurements described next, the \( V_G \) values were applied in the order described above (0 V → +2 V → −1 V → −2 V).

In order to check whether the change in the interfacial MA was dominant in the case of the observed change in the MA, the \( t_{\text{Co}} \) dependence of the effective MA energy was investigated. The results for various \( V_G \) values are shown in Fig. 3(a). The effective MA energy per area \( (t_{\text{Co}}K_u) \) can be expressed as

\[
t_{\text{Co}}K_u = \frac{m_i}{S} \cdot \frac{\mu_0 H_s}{2},
\]

where \( m_i/S \) and \( \mu_0 H_s \) are the saturation magnetic moment per area and the saturation field, respectively. The \( t_{\text{Co}} \) dependence of \( m_i/S \), which was measured directly using the SQUID magnetometer while applying \( V_G \), is shown in Fig. 3(b). The value of \( m_i/S \) increased (decreased) with the application of positive (negative) \( V_G \). The \( \mu_0 H_s \) value was determined from the hard-axis magnetization curves (HAMCs) by using the \( R_{\text{Hall}} \) curve as described in Refs. 11 and 15.
The dashed lines in the saturation magnetic moment per unit area, the HAMCs, whereas the HAMC for points for only the sample with $V = +2$ V, a parallel shifting of the linear dependence of saturation magnetic moment per unit area, $m_s/\mu_0$, for various $V$ values. (c) $t_{Co}$ dependence of saturation magnetic field $\mu_0 H_s$ for various $V$ values. In (b), the filled symbols represent the experimental data whereas the open symbols represent the expected values for the other samples from the linear fittings. The dashed lines in the figures indicate the linear fittings.

$R_{Hall}$ curves for $V_G = +2$, 0, and $-1$ V corresponded to the HAMCs, whereas the HAMC for $V_G = -2$ V was determined by applying an in-plane magnetic field to the sample. The normalized in-plane magnetization ($M_b$) curve for $V_G = +2$ V, which was reproduced from the $R_{Hall} - \mu_0 H_b$ curve, is shown in the inset of Fig. 2. The calculated $t_{Co}$ dependence of $\mu_0 H_s$ for the various $V$ values is shown in Fig. 3(c).

As can be seen from Figs. 3(a)–3(c), the data for $V_G = -2$ V showed a nonsystematic dependence on $t_{Co}$ or a huge change from the data for $V_G = 0$ V. Although the reason for this will be discussed later, we hereafter concentrate on the data for $V_G = +2$, 0, and $-1$ V. Further, in these data, the data points for only the sample with $t_{Co} = 0.48$ nm showed nonsystematic behavior, probably because of the effect of the applied $V_G$ on $T_{Co}$. Therefore, these points were excluded for the linear fittings shown in Fig. 3(a). $t_{Co}K_u$ can be expressed as follows using the interfacial anisotropy energy $K_s$ and the volume (bulk) anisotropy energy $K_v$:

$$t_{Co}K_u = K_v + t_{Co} \cdot \left( K_v - \frac{1}{2} \mu_0 M_s^2 \right),$$

where $M_s$ is the saturation magnetization. Thus, the intercept and slope in the linear fittings in Fig. 3(a) correspond to $K_v$ and $K_v - (1/2)\mu_0 M_s^2$, respectively. For the positive $V_G$ ($+2$ V), a parallel shifting of the linear fit from that for $V_G = 0$ V was observed, indicating that only $K_v$ was modulated (in this case, the modulated $K_v$ was expected to correspond to the change in the Co/MgO interfacial MA). On the other hand, the slope changed from the data for $V_G = -1$ V; however, no clear change in the intercept (i.e., $K_v$) was observed within the experimental error ($\pm 20 \mu J/m^2$). The inset shows the difference in $t_{Co}K_u$ ($t_{Co}K_u = t_{Co}[K_u(V_G) - K_u(0 V)]$) as a function of $t_{Co}$.

The difference in the MA modulation, i.e., $t_{Co}\Delta K_u/\Delta E_G$, where $\Delta E_G$ ($\sim 0.5$ V/nm) is defined as $V_G$ divided by the thickness of the dielectric layer, was $\sim 80 \mu J$ (see Ref. 15) for the details of this calculation; this was comparable to the result obtained at 200 K for a device with an SSC structure and a HfO$_2$ gate insulator at $\Delta E_G \sim 0.4$ V/nm.$^{11}$ The following facts suggest that the observed change in the MA was most likely induced by the charge accumulation effect as long as the Co layer was the cathode ($V_G > 0$): (i) the results obtained in this study were consistent with those obtained in the case of SSCs, (ii) no oxidation was confirmed by the XPS measurements for the as-deposited samples before the application of $V_G$, and (iii) only $K_v$ was modulated by $V_G$. Our result is consistent with that of the previous studies in terms of the fact that the charge accumulation effect is dominant not in the oxidized sample$^{22}$ but rather in the pure metallic sample.$^{28}$
On the other hand, when the Co layer was the anode \((V_G < 0)\), the possibility of the oxidation reaction was required to be considered as discussed in Ref. 3. Figures 4(a)–4(c) show the \(t_{Co}\) dependences of \(t_{Co}K\), \(m_s/S\), and \(\mu_0H_s\), respectively, for the as-deposited samples before and after the OPA treatment. A change in the slope was observed after the OPA treatment; it exhibited the same tendency as that seen when \(V_G\) of \(-1\ V\) was applied to the EDLC. This implies that the phenomenon of anodic oxidation is a possible reason for the electric field effect when \(V_G < 0\). From the \(t_{Co}\) dependence of \(m_s/S\) shown in Fig. 4(b), the following possibilities can be considered: (i) \(M_s\) of the Co layer was independent of its thickness before and after ashing and it reduced after the ashing and (ii) the ratio of the oxidized thickness of the Co layer to the nominal thickness \((t_{Co})\) was independent of \(t_{Co}\) because the intercept of the linear fitting was almost independent of the OPA treatment. Case (ii) may be consistent with the angle-resolved XPS result (pure Co was present inside after the OPA treatment), although the reason the ratio was independent of \(t_{Co}\) is not clear if this is true. In any case, however, the qualitative analysis suggested that the magnitude of the change in the slope in Fig. 4(a) cannot be explained without considering the increase in \(K\), after the OPA treatment. The probable reasons why \(K\) remained nearly unchanged in the above situations are that the anisotropy at the as-deposited Co/MgO interface was much smaller than that at the Pt/Co interface and that the surface oxidation of the Co layer did not induce an additional interfacial effect. We believe that the significant anisotropy at the Co/MgO interface appeared only when the charge accumulation effect was dominant. Finally, we note that the huge change in the magnetic properties at \(V_G = -2\ V\) was probably attributable to the higher degree of oxidation. Oxidation is generally a thermally activated process. Thus, the nonsystematic dependence on \(t_{Co}\) at \(V_G = -2\ V\) might be related to the slight difference in the experimental times.

In summary, the effect of an electric field on the MA in the Pt/Co system was investigated using ionic liquid gating. Charge accumulation was probably the primary mechanism responsible for the change in the MA when the Co layer was the cathode. However, it is likely that oxidation occurred when the Co layer was the anode. Although the approach adopted in this study is an indirect way of evaluating the mechanism responsible for the effect of electric fields on magnetism, it can be considered an intuitive and convenient method for comprehending this mechanism.

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