Fabrication of antiferromagnetic $\alpha$-Cr$_2$O$_3$(0001) thin film and influence on magnetism of ultrathin Co film

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We have investigated the fabrication of $\alpha$-Cr$_2$O$_3$(0001) thin film on a Au(111) surface and the effect of the antiferromagnetic feature of $\alpha$-Cr$_2$O$_3$(0001) on the magnetic properties of ultrathin Co film on $\alpha$-Cr$_2$O$_3$(0001). Highly oriented $\alpha$-Cr$_2$O$_3$(0001) thin film is fabricated by oxidizing Cr(110) thin film grown on a Au(111) surface. Upon the oxidization of threefold symmetric Cr(110) thin film, the $\alpha$-Cr$_2$O$_3$(0001) thin film is produced. On $\alpha$-Cr$_2$O$_3$(0001) thin film, ultrathin Co film is epitaxially grown at 473 K to form fcc-Co(111) film. The antiferromagnetic feature of $\alpha$-Cr$_2$O$_3$ affects the magnetic properties of the ultrathin Co film. Exchange bias is only observed when the magnetic field is applied perpendicular to the film surface, i.e., the direction parallel to the Cr spin. Additionally, in the temperature dependence of magnetization, the clear signature of a Néel temperature of approximately 300 K is observed. The obtained results indicate the collinear coupling of Co and Cr spins.

Key words: Magnetic films, Antiferromagnetic material, Interface phenomena, Epitaxial growth

1. Introduction

Magnetization of a nanosized magnet fluctuates owing to thermal agitation. To suppress the thermal agitation of magnetization, it is necessary to increase effective magnetic anisotropy, which contains a surface/interface contribution as well as a bulk contribution. From this viewpoint, an increase of the effective magnetic anisotropy using the interface effect has been a research area of active pursuit. Among the various types of interface effect, we focus on the interface effect between an antiferromagnet and ferromagnet, known as exchange anisotropy. Recently, it has been reported that the thermal agitation of magnetic nanoparticles in a granular film is suppressed by the exchange anisotropy of a Co/CoO interface.

The exchange anisotropy acts as a source of the effective magnetic anisotropy for increasing the effective magnetic anisotropy. However, since the exchange anisotropy is a unidirectional magnetic anisotropy, there is one energy minimum in the magnetic energy landscape at which the magnetization direction is determined at zero fields. Namely, in this energy landscape, we can stabilize the magnetization in one direction. In the applications such as memory device, two different magnetization directions at zero fields, for example, up and down, correspond to digital information, i.e., 1 and 0, respectively. Thus, it is necessary to change the position of the energy minimum in the magnetic energy landscape to reverse the magnetization direction of a ferromagnet under the exchange anisotropy. This corresponds to controlling the easy direction of the exchange anisotropy. It is well known that the easy direction of exchange anisotropy depends on the spin direction and spin alignment of the antiferromagnetic material at the interface. Thus, to control the easy direction of exchange anisotropy, the spin direction and the spin alignment must be controlled. From this viewpoint, an antiferromagnet having a uniaxial magnetic anisotropy is suitable. $\alpha$-Cr$_2$O$_3$ has a corundum structure, which is an hcp-based crystal structure, and the Cr spin is oriented parallel to the c-axis. These features enable us to alter the spin direction and spin alignment at the interface by altering the crystal orientation of $\alpha$-Cr$_2$O$_3$. Additionally, $\alpha$-Cr$_2$O$_3$ is known to exhibit a magneto-electronic effect: the effect that magnetization is induced by an electric field and vice versa. These promising features of $\alpha$-Cr$_2$O$_3$ allow us to expect that the magnetization direction of the ferromagnet is controllable by using an electric field to control the exchange anisotropy. This concept has recently attracted much attention as a new method for inputting information into magnetic random access memory. Although several mechanisms have been proposed for the origin of the magneto-electronic effect of $\alpha$-Cr$_2$O$_3$, all these mechanisms require the low-symmetry crystal structure of corundum to induce the magneto-electronic effect. Thus, to achieve the above concept, it is essential to fabricate highly oriented $\alpha$-Cr$_2$O$_3$ thin film and to achieve the exchange coupling of $\alpha$-Cr$_2$O$_3$ and a ferromagnetic material at the interface. In our previous report, we demonstrated that $\alpha$-Cr$_2$O$_3$(0001) thin film was successfully fabricated on an $\alpha$-Al$_2$O$_3$(0001) substrate. However, in the previous system, the conductive underlayer which will work as the electrode to apply the voltage to $\alpha$-Cr$_2$O$_3$ is absent. In this study, we report the fabrication of $\alpha$-Cr$_2$O$_3$ thin film on a suitable conductive underlayer. Furthermore, we also report the exchange coupling of $\alpha$-Cr$_2$O$_3$ and a ferromagnetic ultrathin film: Co was chosen as a ferromagnet because it can have an fcc or hcp structure, both of which can be epitaxially grown on $\alpha$-Cr$_2$O$_3$.

2. Experimental procedure

The samples were fabricated by molecular beam epitaxy (MBE) using a VG Semicon V80M multichamber MBE system in which the pressure before deposition was below 5×10$^{-9}$ Pa. Prior to thin film growth, the mirror-polished Si(111) wafer substrate was annealed twice at 1173 K for 120 s to obtain a clean and smooth surface. The surface structures and smoothness were confirmed by reflection.
high-energy electron diffraction (RHEED). Then, a 100-nm-thick Ag(111) buffer layer was grown on the Si(111) substrate at 273 K. The buffer layer was subsequently annealed for 3.6 ks at 673 K to smoothen the surface. Furthermore, a 20.0-nm-thick Au(111) base layer was epitaxially grown on the Ag(111) buffer layer at 373 K as an underlayer for the α-Cr₂O₃ thin film, which was fabricated by oxidizing Cr(110) thin film in high-purity O₂ atmosphere\(^{11}\). The 20.0-nm-thick Cr(110) thin film was grown on the Au(111) base layer at 373 K. Then, the sample was transferred to the oxidation chamber in the MBE multichamber system and was annealed for 1.8 ks at 1073 K in a high-purity O₂ gas flow. The O₂ gas pressure during the annealing was fixed at 3×10⁻⁸ Pa. After transferring the sample back to the growth chamber, 2.3-nm-thick Co was grown on the α-Cr₂O₃ thin film at 273 K. Since some of structural and magnetic characterizations were performed after removing the sample from the UHV chamber, the samples were exposed to air. To avoid the surface oxidization of Co, a 4.0-nm-thick Cr film and 6.0-nm-thick Au film were deposited on the ultrathin Co film at 293 K.

RHEED observations were conducted in-situ at 30 kV with an incident angle of about 1° to characterize the surface structure of each layer and substrate. The crystal orientations perpendicular to the film surface were determined from the RHEED observations. The relationship between the crystal orientation among the Si substrate, Au base layer and α-Cr₂O₃ thin film was determined by X-ray diffraction (XRD). Magnetization measurements were performed by superconducting quantum interference device (SQUID) magnetometry. Our investigation encompassed the magnetization curve, and the temperature dependence of magnetization in the temperature range of 5 to 340 K. Both types of measurements were carried out after field-cooling (FC) and zero-field-cooling (ZFC). The measurements were performed during the heating process after the sample was cooled from 340 to 5 K. Note that a Néel temperature of bulk α-Cr₂O₃ is reported to be about 307 K\(^{12}\).

3. Results

3.1 Structure of α-Cr₂O₃(0001) thin film

An oxide film formed on a metal is not always crystallized but sometimes becomes amorphous or poly crystalline. Actually, we previously reportted\(^{11}\) that in case of Cr(110) thin film on a α-Al₂O₃(0001) substrate, the crystalline quality of Cr oxide film is strongly dependent on the crystallographic orientation of the Cr(110) thin film before the oxidation. In particular, it was found that well-defined α-Cr₂O₃(0001) thin film was obtained by oxidizing three fold symmetric Cr(110) thin film, whereas the Cr oxide film was poly crystalline when Cr(110) thin film with more than the six fold in-plane symmetry was oxidized. This structural change is explained by the epitaxial relationship between α-Cr₂O₃(0001) and Cr(110): Nishiyama-Wassermann (NW) relationship. In this study, 20.0-nm-thick Cr is deposited on Au(111), which allow us to expect that Cr(110) thin film grows on the Au(111) base layer with NW or Kurdjumov-Sachs (KS) relationship. The NW relationship between Cr(110) and Au(111) was reported in previous paper\(^{13}\). In contrast, in our case RHEED pattern of Cr(110) film grows on the Au(111) base layer (not shown) indicates the KS relationship with Au(111). RHEED patterns and corresponding key diagrams after the oxidation of Cr(110) thin film are shown in Fig. 1. Well-defined diffraction spots are clearly observed for different electron-beam incidences, indicating the formation of α-Cr₂O₃(0001) thin film. In addition, the RHEED pattern and schematic diagram in Fig. 1(b) indicate that our α-Cr₂O₃(0001) thin film contains a twin boundary parallel to the [1 1 0] direction. Weak diffraction spots are observed between the strong spots in Fig. 1(a). Since the RHEED pattern with [1 1 0] azimuth is sensitive to the site occupation of oxygen ions\(^{14}\), these spots are probably generated by the incorrect occupation of oxygen ions. However, the origin of these spots is unclear at present.

Since the quantitative determination of the relationship between crystal orientation among the α-Cr₂O₃(0001) thin film, Au(111) base layer and Si(111) substrate is difficult from RHEED observations, the in-plane XRD profiles are measured. Figs. 2(a)-2(c) show the in-plane XRD profiles for diffraction from Cr-Cr₂O₃(1 0 1 4), Au(200) and Si(400), respectively. In the XRD profiles corresponding to α-Cr₂O₃(1014) diffraction and Au(200) diffraction, six diffraction peaks are observed, indicating the formation of a twin. For α-Cr₂O₃(1014) diffraction, the amount of the two sets of domains comprising the twin is almost the same because the six diffraction peaks have almost the same intensities. In contrast, for Au(200) diffraction, the diffraction intensities are different for the two domains comprising the
twin, meaning that one is the major domain and the other is the minor domain. This means that the formation of twin domains in α-Cr₂O₃(0001) thin film is not caused by their information in the formation twins in the underlying Au(111) base layer but is an inherent feature of α-Cr₂O₃ thin film.

It can also be seen in Figs. 2(a) and 2(b) that the peak positions of α-Cr₂O₃(11̄04) diffraction are shifted by 30° from those of Au(200) diffraction and Si(400) diffraction. From the results of RHEED observations and XRD profiles, the epitaxial relationship between the α-Cr₂O₃(0001) thin film, Au(111) base layer and Si(111) substrate is given as follows.

α-Cr₂O₃(0001)<11̄00> // Au(111)<11̄0> // Si(111) <11̄0>

The relationship between the orientation of the α-Cr₂O₃(0001) thin film and Au(111) base layer is schematically represented in Fig. 2(d). Lattice misfit of 0.8% is obtained at the interface between the α-Cr₂O₃(0001) thin film and Au(111) base layer assuming bulk lattice parameters.

Since α-Cr₂O₃ is a line compound, it is possible that unoxidized Cr remains or that metallic Cr precipitates in α-Cr₂O₃ if the oxidation is incomplete. We have confirmed that our α-Cr₂O₃ has a single phase and that unoxidized Cr does not remain in α-Cr₂O₃ from cross-sectional TEM images (not shown).

### 3.2 Magnetism of ultrathin Co film on α-Cr₂O₃(0001)

Prior to discussing the magnetic properties of ultrathin Co film, we briefly mention the structure of Co film. The 2.3-nm-thick Co film was grown epitaxially on α-Cr₂O₃(0001) thin film. RHEED patterns of the Co film are shown in Fig. 3. Although it is difficult to distinguish fcc(111) from hcp(0001), it is possible to do so from the RHEED patterns for the [112] azimuth. As shown in the key diagram, the RHEED patterns are indexed by fcc(111) with the twin boundary parallel to the [112] direction, and thus Co forms twinned fcc-Co(111). The epitaxial growth of Co on α-Cr₂O₃ indicates that the chemical bonding of Co and α-Cr₂O₃(0001) is achieved. Additionally, the diffraction patterns from the α-Cr₂O₃(0001) surface are dimly observed in the RHEED pattern in Fig. 3(b), meaning that a small amount of α-Cr₂O₃(0001) surface is still exposed within the electron penetration depth.

As a first result for the magnetic properties, the appearance of exchange bias and its dependence on applied field direction are reported. Figs. 4(a) and 4(b) shows the magnetization curves measured at 5 K after FC (●) and ZFC (○). The applied field direction is parallel to the film surface, [112] of Si(111) substrate. Magnetization saturates below 5 kOe, and a large coercivity of about 1 kOe and a remanence ratio of about 0.7 are observed. These features mean that...
the in-plane direction is the easy direction of magnetization. However, the exchange bias is not observed even after FC. It is known that the exchange bias is affected by the spin structure of the antiferromagnetic layer at the interface. In particular, since our fabricated Cr$_2$O$_3$ thin film has the <0001> orientation perpendicular to the film plane, as shown in the previous section, it is expected that the Cr spin has anisotropic spin alignment in the Cr$_2$O$_3$(0001) thin film. Thus, the applied field direction might affect the appearance of the exchange bias effect. The magnetization curves at 5 K in the direction perpendicular to the film are shown in Figs. 5(a) and 5(b). It can be seen that the magnetization saturates at a higher field ~20 kOe, and both coercivity and remanence ratio are lower than those in the direction parallel to the film plane. These features indicate that the direction perpendicular to the film is the magnetic hard axis. It is also observed that the magnetization linearly increased above 20 kOe, even after the background signal is carefully subtracted. The linear increase in magnetization at the high magnetic field is not observed for ultrathin Co film on α-Al$_2$O$_3$(0001) (see below, Fig. 7). Therefore, it is thought to originate from the anisotropic spin alignment of the fabricated α-Cr$_2$O$_3$(0001) thin film. Additionally, even when the magnetic field is applied perpendicular to the film, the magnetization of Co saturates at a low field relative to the anisotropy field of fcc-Co, indicating that a certain type of magnetic anisotropy is induced in the direction perpendicular to the film. Furthermore, as can be seen in Fig. 5(b), a shift of the magnetization curve after FC is clearly observed, and an exchange bias field of about 500 Oe is obtained.

The shift of the magnetization curve, namely, the exchange bias effect, is observed only in the direction perpendicular to the film and is not observed parallel to the film. The appearance of exchange bias perpendicular to the film surface is explained by the spin direction of the Cr ions in α-Cr$_2$O$_3$(0001) thin film. As mentioned in Section 1, Cr spins lie parallel to the c-axis in bulk α-Cr$_2$O$_3$. Thus, the Cr spin in our α-Cr$_2$O$_3$ thin film can align in the direction perpendicular to the film surface owing to the <0001> orientation perpendicular to the film. By considering the expected Cr spin direction, the above-mentioned results indicate that the additional interface anisotropy is induced in the direction parallel to the Cr spin direction. Supporting this discussion, Dho et al., reported that the exchange bias was observed in the direction parallel to the Cr spin for poly

Fig. 4. Magnetization curves of 2.3-nm-thick Co film on α-Cr$_2$O$_3$(0001). The applied field direction is parallel to film, [11 2 |] direction of Si(111) substrate. The measurement temperature is 5 K. The solid and open circles represent the field-cooled (FC) and zero-field-cooled (ZFC) magnetization, respectively. Fig. 3(b) shows the enlarged figure of (a).

Fig. 5. Magnetization curves of 2.3-nm-thick Co film on α-Cr$_2$O$_3$(0001). The applied field direction is perpendicular to film, and the measurement temperature is 5 K. The solid and open circles represent the field-cooled (FC) and zero-field-cooled (ZFC) magnetization, respectively. Fig. 4(b) shows the enlarged figure of (a).
the antiferromagnetic order of Co and Cr spins at the interface is collinear. To address this issue, the temperature dependence of magnetization is investigated. Fig. 6 shows the temperature dependence of magnetization under the magnetic field of 50 Oe after FC and ZFC. As shown in Fig. 6(a), FC magnetization is almost constant below 50 K, gradually increases up to 175 K, starts to decrease from approximately 175 K, and then rapidly drops to zero at 300 K. On the other hand, the magnetization after ZFC is almost zero in the entire temperature range except for a small peak at 300 K. These features clearly indicate that the antiferromagnetic feature of α-Cr2O3 affects the magnetic behavior of Co. Namely, the additional magnetic anisotropy is induced parallel to the Cr spins owing to the collinear coupling of Co and Cr spins. With increasing temperature, the antiferromagnetic order of α-Cr2O3 is weakened, and when the temperature reaches the Néel temperature, the induced magnetic anisotropy vanishes owing to the fluctuation of the Cr spin direction. In fact, above 300 K the magnetization in the direction perpendicular to the film drops to almost zero while the in-plane magnetization remains, probably owing to the shape anisotropy (Fig. 6(b)).

The signature of the Néel temperature appears in the temperature dependence of magnetization in the direction parallel to the film. As shown in Fig. 6(b), the peak at approximately 300 K is superimposed on the curve for both FC and ZFC magnetizations. These peaks reflect the Néel temperature of the fabricated Cr2O3 thin film.

Here, we mention the possibility of biquadratic coupling at the interface as the other magnetic coupling at the interface. As shown in Figs. 4 and 6(b), the magnetic easy direction of the 2.3-nm-thick Co film lies in the film plane. As briefly mentioned above, this is probably because the continuous film structure gives rise to the in-plane shape anisotropy. In addition to the shape anisotropy, biquadratic coupling at the interface can promote the in-plane magnetic anisotropy. It is known that biquadratic coupling is generated by the interface roughness. In fact, as shown in Fig. 1, the RHEED pattern of our Cr2O3(0001) thin film is spotty, indicating that the surface of Cr2O3(0001) thin film is not very smooth. It is emphasized the presence of biquadratic coupling does not contradict the absence of the exchange bias in the film plane. According to previous reports, the biquadratic coupling contributes only to the enhancement of coercivity and does not contribute to the exchange bias. The presence of biquadratic coupling at the interface will be verified by further investigations, i.e., the temperature dependence of coercivity and exchange bias, research on a discontinuous film where the shape anisotropy is weakened, and the influence of magnetic anisotropy direction of ultrathin magnetic film.

4. Discussions

Here, we discuss the effect of lattice strain on the antiferromagnetic feature of α-Cr2O3(0001) thin film. The spin alignment of an antiferromagnetic material is sometimes affected by lattice strain. In particular, for the epitaxial thin film system, the lattice parameter of the thin film can trace that of the underlying layer. Thus, our α-Cr2O3(0001) thin film can change its spin arrangement by the lattice strain. As discussed in the previous section, our α-Cr2O3(0001) thin film has a good epitaxial relationship with the Au(111) base layer. Assuming the bulk lattice parameters, a lattice misfit of about 0.8% is obtained. This value is quite small, and it implies that the spin alignment of our α-Cr2O3(0001) thin film is similar to that of bulk α-Cr2O3. This discussion is verified by the results for the α-Cr2O3(0001) thin film prepared on the different underlayers. In our previous report, α-Cr2O3(0001) thin film was fabricated on an α-Al2O3(0001) substrate, in which the lattice misfit was about 4.0% assuming the bulk lattice parameters. In the previous paper, we reported that the Néel temperature of α-Cr2O3(0001) thin film on an α-Al2O3(0001) substrate was approximately 270 K which is about 40 K lower than that of bulk α-Cr2O3, while the Néel temperature of α-Cr2O3 fabricated in this work is about 300 K as shown in Fig. 6. The large decrease in the Néel temperature of α-Cr2O3(0001) thin film on the α-Al2O3(0001)
substrate indicates the disturbance of the spin alignment of α-Cr$_2$O$_3$ due to the large lattice misfit. As results supporting the altered spin alignment of α-Cr$_2$O$_3$, the magnetization curves of 1.0-nm-thick Co film grown on α-Cr$_2$O$_3$(0001) thin film with an α-Al$_2$O$_3$(0001) substrate are shown in Fig. 7. The applied field direction is (a), (b) perpendicular and (c), (d) parallel to the film plane. The curves were measured at 5 K. It can be seen that no exchange bias is observed for both applied field directions. The absence of exchange bias implies that the spin alignment of α-Cr$_2$O$_3$(0001) thin film is disturbed at the interface. The above differences between the α-Cr$_2$O$_3$(0001) thin film grown on the Au(111) base layer and that on the α-Al$_2$O$_3$(0001) substrate strongly indicate that the α-Cr$_2$O$_3$(0001) thin film on the Au(111) base layer has a similar spin alignment to the bulk owing to the good lattice matching. We believe that the good lattice matching and the small lattice distortion result in the appearance of the exchange bias.

We have investigated the fabrication of α-Cr$_2$O$_3$(0001) thin film on a conductive underlayer toward the utilization of the magneto-electronic effect. The exchange coupling of an α-Cr$_2$O$_3$(0001) thin film and an ultrathin Co film has also been investigated. On the Au(111) base layer, well-defined α-Cr$_2$O$_3$(0001) thin films are successively fabricated. The fabricated α-Cr$_2$O$_3$(0001) thin film has a good epitaxial relationship with the underlying Au(111) base layer and the Si(111) substrate. The magnetic behavior of a 2.3 nm-thick Co film grown on α-Cr$_2$O$_3$(0001) thin film is strongly affected by the antiferromagnetic feature of α-Cr$_2$O$_3$. In particular, the exchange bias is observed only in the direction parallel to the Cr spin. The observed features indicate that Co and Cr spins couple collinearly at the interface.

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