Superparamagnetism of ultrathin Co film on antiferromagnetic Cr$_2$O$_3$ layer

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Abstract. The effect of antiferromagnetic Cr$_2$O$_3$ thin film on the magnetic properties of ultrathin Co film has been investigated. To achieve the investigation, we have also investigated the fabrication of Cr$_2$O$_3$ thin film of high quality using MBE. The crystalline quality of Cr oxide film strongly depends on the in-plane epitaxial variants of Cr(110) before the oxidation. We have successfully fabricated Cr$_2$O$_3$(0001) film by oxidizing three fold-symmetric Cr(110) film. On Cr$_2$O$_3$(0001) thin film, the magnetization of Co is stabilized parallel to the Cr spin direction below the Néel temperature of Cr$_2$O$_3$.

1. Introduction

Magnetization of nano-magnets essentially fluctuates due to the thermal agitation [1]. Since the thermal agitation of magnetization makes the magnetization direction difficult to fix to the certain direction, it is recognized the problem to overcome for the device application of nano-magnets. The thermal agitation of magnetization is often discussed using the ratio $\Delta E/k_B T$, where $\Delta E$ is the energy barrier for the magnetization reversal, $k_B$ is the Boltzmann constant and $T$ is the absolute temperature. For $\Delta E/k_B T \ll 25$, the net magnetization vanishes, namely the nano-magnet is in the superparamagnetic state. Since $\Delta E$ is expressed by the effective magnetic anisotropy and the volume of magnetic entity through the relationship $\Delta E = K_{eff} \cdot V$, in order to suppress the thermal agitation of magnetization in keeping the volume in the nano-size, it is necessary to increase the effective magnetic anisotropy $K_{eff}$. $K_{eff}$ includes the surface/interface anisotropy as well as the bulk anisotropy like the magneto-crystalline anisotropy. Especially, for the nano-magnets, the surface/interface anisotropy can dominate $K_{eff}$ owing to the large surface/interface contribution. In this viewpoint, we have investigating the control of magnetism of nano-magnet using the interface anisotropy. Among the various surface/interface effect, we utilize the interface effect between the antiferromagnet and the ferromagnet, known as the exchange anisotropy. Since it is well known that the exchange anisotropy depends on the spin direction of antiferromagnetic layer [2, 3], in order to clarify the detailed effect of antiferromagnetic layer, it is suitable to use the antiferromagnet in which the spin direction is controllable. In this study, we chose Cr$_2$O$_3$ as an antiferromagnet because Cr$_2$O$_3$ has the highly anisotropic crystal structure and thus, the spin direction could be controlled by altering crystallographic orientation. Especially for thin film system, controlling crystallographic orientation is easily possible by using epitaxial growth. In this report, using Co as a ferromagnet we report the effect of antiferromagnetic Cr$_2$O$_3$ layer on the magnetic properties of ultrathin Co film.

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α-Cr$_2$O$_3$ has the corundum structure which is consisted by 12 Cr layers and 6 O layers. Corundum structure is schematically shown in figure 1. In each Cr layer, the spin orients parallel to c axis and is antiferromagnetically aligned in the neighboring Cr layer. This implies that for α-Cr$_2$O$_3$ thin film, the spin alignment at the surface/interface is controllable by changing crystallographic orientation. In fact, it has been reported that both the strength and symmetry of exchange anisotropy is changed by altering crystallographic orientation of Cr$_2$O$_3$ for the polycrystalline permalloy / Cr$_2$O$_3$ bilayer in which the crystallographic orientation of Cr$_2$O$_3$ is altered by (0001), ⟨1120⟩ and ⟨1102⟩ [4].

As mentioned above, Cr$_2$O$_3$ is an antiferromagnet, and it is known that Cr$_2$O$_3$ shows the magneto-electronic (ME) effect, as well [5]. ME effect means that the magnetization is induced by applying electronic field. ME effect of Cr$_2$O$_3$ is originated from the combined effects of the low crystallographic symmetry due to the corundum structure and the c-axis oriented Cr spin. Owing to the recent progress in spin-electronics, controlling magnetism using the electronic field has attracted attention, and ME effect of Cr$_2$O$_3$ is also being the subject of intense research activity [6-8]. Change of exchange bias by the ME effect of Cr$_2$O$_3$ has been experimentally observed for Co/Pt superlattice on Cr$_2$O$_3$(111) substrate [6]. However, in this report, since Cr$_2$O$_3$ is utilized as 0.7 mm-thick substrate, the required voltage for ME effect is quite large, and it would be necessary to observe ME effect using Cr$_2$O$_3$ thin film for the device application.

For the control of antiferromagnetic spin alignment and the utilization of ME effect, it is necessary to fabricate the Cr$_2$O$_3$ thin film of high quality. In this report, we have also investigated the fabrication of highly oriented Cr$_2$O$_3$ thin film using Molecular Beam Epitaxy (MBE) system.

2. Experimental

2.1. Sample preparation
Cr oxide thin films were prepared by oxidizing Cr thin film in ultra-high-vacuum (UHV) chamber. Cr thin films before the oxidation was prepared by VG-80M molecular beam epitaxy (MBE) system. The base pressure before and during growth was typically below $4 \times 10^{-9}$ and $5 \times 10^{-8}$ Pa, respectively. The deposition temperature of Cr was varied 323 to 473 K. The thickness of Cr before oxidation was fixed.
to 20 nm. Three types of \( \alpha \)-Al\(_2\)O\(_3\) surfaces having (0001), (1\(\bar{1}\)20), and (\(\bar{1}\)02) were used as the substrate, because \( \alpha \)-Al\(_2\)O\(_3\) has the corundum structure same to \( \alpha \)-Cr\(_2\)O\(_3\). The substrate was annealed in air at 1273 K to flatten the surface before introducing the vacuum system. After that, it was cleaned in UHV chamber by annealed for several hours at 1173 K prior to the Cr deposition.

After depositing Cr, the samples were transferred to the oxidation chamber, which is connected to the growth chamber under UHV, without exposing air. At the oxidation chamber, Cr thin film was oxidized by annealing at 973 K in O\(_2\) of 3\(\times\)10\(^{-3}\) Pa. Note that the pressure of oxidation chamber before introducing O\(_2\) was below 9\(\times\)10\(^{-9}\) Pa.

Then, the sample was again transferred to the growth chamber, and Co was deposited on the oxidized Cr film at 473 K by MBE. The thickness of Co is fixed to 1.0 nm. To investigate the magnetic properties mentioned below, the films have to be exposed to air. In order to prevent the surface oxidation, 10 nm-thick Au capping layer was deposited on Co at room temperature.

### 2.2. Structural and magnetic characterization

The structure of thin films was investigated using reflection high energy electron diffraction (RHEED) and X-ray diffraction (XRD). Investigation using RHEED were performed \textit{in-situ} at growth chamber. Observation of RHEED was carried out at 30 kV with an incident angle 1°. XRD profiles were obtained in polar (\(\phi\)) scan for the quantitative investigation of crystal structure.

Magnetization measurements of thin films were performed by superconducting quantum interference (SQUID) magnetometry. Our investigation encompassed the temperature dependence of field-cooled (FC), ZFC, and remanent (RM) magnetization in the temperature range of 5 to 300 K under the magnetic fields of 50 Oe. The measurements were performed during the heating process. Especially, two types of RM are measured after FC and ZFC, called as the thermo-remanent magnetization (TRM) and the isothermal remanent magnetization (IRM), respectively [9, 10]. For instance, when TRM was measured, the sample was cooled from the enough high temperature, R.T. to the measurement temperature under the certain field. After reaching measurement temperature, the field was removed and the magnetization was measured. In the case of IRM, the similar procedure was done after ZFC procedure. TRM and IRM give the stable magnetization after removing field and the activated magnetization by applying field, respectively.

### 3. Results and Discussions

#### 3.1. Structure of Cr oxide thin film

The crystalline quality of Cr oxide film depends on the surface structure of Cr thin film before oxidization. RHEED patterns of Cr thin film before and after oxidization are shown in figure 2. In our preparation method described in Section 2.1, all studied Cr thin films before oxidation possess bcc structure with (110) orientation perpendicular to the film plane. However, the in-plane crystallographic symmetry due to the epitaxial variants changes by the growth condition. In this work, two types of growth are observed. One is shown as RHEED pattern shown in figure 2(a); the formation of three-fold symmetric Cr(110). This growth manner is observed only for Cr grown on \( \alpha \)-Al\(_2\)O\(_3\)(0001) and \( \alpha \)-Al\(_2\)O\(_3\)(1\(\bar{1}\)20) at 473 K. The other growth manner is the formation of Cr(110) variants having more than six variants, shown in figure 2(b). The latter growth occurs for Cr grown on \( \alpha \)-Al\(_2\)O\(_3\)(01\(\bar{1}\)0) and Cr on \( \alpha \)-Al\(_2\)O\(_3\)(0001) and \( \alpha \)-Al\(_2\)O\(_3\)(1\(\bar{1}\)20) at 323 K.

RHEED pattern of Cr oxide thin film are strongly depends on the number of Cr(110) variants before oxidization. As shown in figure 2(c), the clear diffraction spots are observed by oxidizing Cr(110) having three variants. The observed patterns are well matched to the expected reciprocal lattice map of the corundum structure. Since RHEED observation is not suitable for the quantitative analysis, the quantitative information of crystal structure is obtained from the XRD measurement. As a result, adopting Bragg condition for \( \alpha \)-Cr\(_2\)O\(_3\)(1\(\bar{1}\)04), the distinct diffraction peak are observed in \(\phi\).
scan with the six fold-symmetry (not shown). However, \( \alpha\text{-Cr}_2\text{O}_3(\overline{\text{1}04}) \) diffraction show the three fold-symmetry for the single crystalline \( \alpha\text{-Cr}_2\text{O}_3 \), and thus our film should form the twinned structure. These results strongly suggest that the fabricated Cr oxidized thin film is the twinned \( \alpha\text{-Cr}_2\text{O}_3(0001) \) thin film.

![Image](image1.png)

**Figure 2.** [11\(2\)0]\(\alpha\text{-Al}_2\text{O}_3\)-azimuthal RHEED patterns of Cr thin film (a), (b) before and (c), (d) after oxidation. The results are on 20.0 nm-thick Cr grown on \( \alpha\text{-Al}_2\text{O}_3(0001) \) substrate at the different temperature.

On the contrary, as shown in figure 2(d), RHEED patterns are the ring pattern by oxidizing Cr(110) having more than six variants. This means that the Cr oxide films are poly-crystalline. In this case, since the quantitative analysis is difficult as explained above, the crystal structure is not determined.

Here, the reason for the formation of \( \alpha\text{-Cr}_2\text{O}_3(0001) \) by oxidizing three fold-symmetric Cr(110) is discussed. The formation of \( \alpha\text{-Cr}_2\text{O}_3(0001) \) is explained by the epitaxial relationship between \( \alpha\text{-Cr}_2\text{O}_3(0001) \) and Cr(110). The atom arrangements of \( \alpha\text{-Cr}_2\text{O}_3(0001) \) and Cr(110) are schematically represented in figure 3. \( \alpha\text{-Cr}_2\text{O}_3(0001) \) lattice and Cr(110) lattice is matched in following orientation.

\[ \alpha\text{-Cr}_2\text{O}_3(0001) \langle\overline{\text{1}100}\rangle // \text{Cr}(110)\langle001\rangle \]

In this orientation, the lattice misfit is 0.70% assuming lattice constant of bulk value. This orientation relationship is similar to the Nishiya-Wassermann relationship which is well known as that of fcc(111) and bcc(110). Note that fcc(111) and hcp(0001) have the identical atom arrangement in topmost layer, and thus the appearance of similar relationship is reasonable. This result implies that

![Image](image2.png)

**Figure 3.** Scheme of orientation relationship between \( \alpha\text{-Cr}_2\text{O}_3(0001) \) and bcc Cr(110). Assuming the bulk value as the lattice constant, the lattice misfit is 0.70 % for the shown orientation relationship.(colour online)
the formation of α-Cr₂O₃ having the specific orientation requires the suitable atomic arrangement of Cr before oxidation. In other words, controlling the crystallographic orientation of α-Cr₂O₃ thin film, namely spin arrangement at interface would be possible by changing the orientation of Cr film before oxidation.

3.2. Magnetic properties of ultrathin Co film on Cr₂O₃(0001) thin film

Before investigating the effect of Cr spin direction on the magnetic properties of ultrathin Co film, the magnetic state of Co at room temperature is shown. Magnetization curve and temperature dependence of magnetization of ultrathin Co film grown on Cr₂O₃(0001) are shown in figure 4. The magnetic field was applied parallel to the film plane. In the magnetization curve at room temperature, neither remanent magnetization nor coercivity is observed, and the magnetization is hard to saturate above 20 kOe (figure 4(a)). Furthermore, in the temperature dependence of magnetization, the clear deviation of FC magnetization and ZFC magnetization is observed below 200 K (figure 4(b)). These results indicate that the magnetization of Co at room temperature is highly fluctuated due to the thermal energy. However, the magnetic properties shown in figure 4, especially the temperature dependence of magnetization contain the distinct difference from the ideal superparamagnet. In figure 4(b), the peak of magnetization is observed in both FC magnetization and ZFC magnetization, while the peak would appear only in ZFC magnetization for the ideal superparamagnet. The observed peaks are explained by considering that the peak is originated from Néel temperature of the fabricated Cr₂O₃ thin film. Assuming that the Cr spin direction in the fabricated Cr₂O₃ thin film is parallel to c-axis, the in-plane magnetic field means the perpendicularly applied field to the Cr spin direction. In the case, FC magnetization and ZFC magnetization below Néel temperature would orient to perpendicular to the film plane, reflecting the under-lying Cr spin direction. Increasing temperature and approaching Néel temperature, the magnetization of Co rotate to the applied field direction owing to the weakened antiferromagnetic order of Cr spin. Based on this discussion, it is considered that the peak in FC magnetization and ZFC magnetization is recognized as the Néel temperature of the fabricated Cr₂O₃ thin film.

The above discussion would be verified from the temperature dependence of magnetization in which the magnetic field is applied perpendicularly the film plane, namely parallel to the expected Cr spin direction. Figure 5 show the temperature dependence of FC magnetization, ZFC magnetization, TRM and IRM. As shown in

![Figure 4](image1.png)

**Figure 4.** (a) Magnetization curve measured at room temperature and (b) temperature dependence of magnetization for 1.0 nm-thick Co film on Cr₂O₃(0001). The magnetic field is applied parallel to the film plane.

![Figure 5](image2.png)

**Figure 5.** Temperature dependence of (a) FC magnetization and ZFC magnetization, (b) TRM and IRM. for 1.0 nm-thick Co film on Cr₂O₃(0001). The magnetic field is applied perpendicular to the film plane.
According to the above discussion, the field parallel to the Cr spin would not cause the magnetization rotation around the Néel temperature for FC magnetization. Hence, the observed feature agree with the above discussion. Furthermore, as shown in figure 5(b), TRM and IRM are completely identical to FC magnetization and ZFC magnetization below the Néel temperature, respectively. These results indicate that the magnetization of Co is stable for the Cr spin direction below the Néel temperature even after removing field. In fact, above the Néel temperature when the antiferromagnetic order of Cr spin is destroyed, TRM(IRM) deviate from FC(ZFC) magnetization, and decrease rapidly, respectively.

As mentioned above, while the magnetization of Co on Cr$_2$O$_3$(0001) thin film is stabilized parallel to the Cr spin direction below the Néel temperature, Co rapidly becomes the superparamagnetic state above the Néel temperature. Considering that the blocking temperature of Co grown on $\alpha$-Al$_2$O$_3$(0001) substrate is approximately 90 K [11], the ferromagnetic state above 100 K for Co on Cr$_2$O$_3$(0001) would be caused by the antiferromagnetic order of Cr$_2$O$_3$. However, since the magnetic state of nano-magnets is influenced by the nano-structure such as the particle and the continuous film, the further detailed investigation, especially the correlation to the nano-structure is necessary.

4. Summary

The fabrication of Cr$_2$O$_3$ thin film using MBE system and the magnetic properties of ultrathin Co film on Cr$_2$O$_3$ have been investigated. The crystalline quality of Cr oxide film is affected by the epitaxial growth of Cr film before oxidation. $\alpha$-Cr$_2$O$_3$(0001) are fabricated by oxidizing Cr(110) film having the three equivalent in-plane variants. The formation of $\alpha$-Cr$_2$O$_3$(0001) is explained by the epitaxial relationship known as Nishiyama-Wasserman relationship. Using fabricated $\alpha$-Cr$_2$O$_3$(0001) film, the effect of Cr spin on the magnetic properties of Co has been examined. In $\alpha$-Cr$_2$O$_3$(0001), Cr spin would align perpendicular to the film plane, and the aligned Cr spin affect the magnetic properties of ultrathin Co film. The magnetization direction of Co is stabilized to the Cr spin direction below the Néel temperature which is approximately 280 K in our case. Above the Néel temperature, decreasing antiferromagnetic order of Cr spin, the magnetization of Co starts to fluctuate against the thermal agitation and Co become superparamagnetic. Comparing results to that of Co on $\alpha$-Al$_2$O$_3$(0001), it is considered that the magnetization of Co is stabilized by the antiferromagnetic spin of Cr.

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