

# IMPROVEMENT OF R-PLANE ORIENTED Cr<sub>2</sub>O<sub>3</sub> THIN FILMS SURFACE GROWN ON SAPPHIRE SUBSTRATES

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## Introduction

Cr<sub>2</sub>O<sub>3</sub> is a classical magnetoelectric (ME) material with the Néel temperature ( $T_N$ ) at 308K. The ME effect is characterized as a induction of magnetization by means of an electric field and induction of polarization by means of a magnetic field. Since the materials of *e.g.* TbMnO<sub>3</sub>, BiMnO<sub>3</sub>, BiFeO<sub>3</sub> (BFO) and so on, are recognized as a multiferroic material, which is defined as two or more of the primary ferroic properties are united in the same phase, related materials as well as novel functional devices are energetically investigated. However almost all of the multiferroic materials are ferroelectric (FE) but antiferromagnetic (AF), therefore horizontal heterostructures and/or nanopillars structures with a ferromagnetic (FM) and a piezoelectric materials are prepared in order to obtain FM and FE multiferroic. The novel devices, magnetoelectric random access memory (MERAM) and logic cell using MERAM, are introduced with the exchange bias ( $H_{EB}$ ) in the multilayer of AF-ME and FM materials [1]. However the heating above  $T_N$  and magnetic and electric field cooling are required to control the FM order. In those systems, the Cr<sub>2</sub>O<sub>3</sub> and the BFO are often used because the  $T_N$  of Cr<sub>2</sub>O<sub>3</sub> and BFO, and FE Curie temperature ( $T_{CE}$ ) are above room temperature. In the device using the  $H_{EB}$ , the magnetic exchange interaction at the interface is significant parameter as demonstrated in the well-known Meiklejohn-Bean formula (1), where  $J$ ,  $S_{AF}$ ,  $S_{FM}$ ,  $M_{FM}$ , and  $t_{FM}$  denote the interfacial exchange, the excess interface moments of the AF and the FM components, the magnetization, and the thickness of the FM component, respectively [1].

$$\mu_0 H_{EB} = -\frac{JS_{AF}S_{FM}}{M_{FM}t_{FM}} \quad (1)$$

Since the film surface definitely show step-terrace structure even though the crystallinity of the grown films are perfectly single crystal. The spin structure of the BFO film surface is expected to be AF due to the presence of the steps, and then the  $S_{AF}$  cancels out, while the  $r$ -surfaces at all terraces induced by the presence of steps in the Cr<sub>2</sub>O<sub>3</sub> show the FM spin structure in the state of aligned AF domain by the magnetic and electric field cooling [2]. Such the FM ordering at the surface is not realized in any other perovskite related structures.

In our previous studies, the optimized condition of substrate temperature ( $T_S$ ), introduced gas, and pressure

while growth on  $r$ -,  $a$ -, and  $c$ -cut sapphire is 580°C, O<sub>2</sub>/Ar = 2 / 8 ccm, 0.2-0.3Pa, where epitaxial growth is demonstrated by a x-ray diffraction (XRD), a reflection high energy electron diffraction (RHEED), and a scanning probe microscopy (SPM) [3,4]. However, the film surface grown on  $r$ -cut sapphire shows holes with tens nm in depth between grains although we can find the unit step and terraces structure in one grain. Those holes must be removed. Increasing the  $T_S$ , the film surface becomes rough and oxygen deficient Cr<sub>2</sub>O<sub>3-x</sub> grows investigated by x-ray photoelectron spectroscopy (XPS). In this research we focus on the realization of a smooth surface with unit atomic step in the  $r$ -plane oriented Cr<sub>2</sub>O<sub>3</sub> thin films in order to obtain the large  $S_{AF}$ .

## Experimental

The Cr<sub>2</sub>O<sub>3</sub> films were grown by off-axis DC-RF magnetron sputtering method with two-inch Cr metal target on the  $r$ -cut sapphire substrates. All substrates were annealed at 1000°C for 12 h in air in advance. The  $T_S$  was measured by pyrometer through a ZnSe view port just before growth. The relationship between the temperatures of substrate surface measured by K-thermocouple and the temperature measured by pyrometer was detected for the accurate substrate surface temperature in advance. The DC current and RF power were 0.04A and 80W. The  $T_S$ , sputtering gas, and growth pressure are summarized in Table 1. After the deposition of the film for two hours, oxygen gas was introduced up to 0.1MPa immediately and then the grown films were cooled down.

Table 1 Growth condition of the Cr<sub>2</sub>O<sub>3</sub> thin films by DC-RF magnetron sputtering method.

	$T_S$ (°C)	580	620	660
O <sub>2</sub> /Ar ratio				
2.0 (24 / 12 ccm)		–	–	0.47Pa
1.0 (12 / 12 ccm)		–	0.40Pa	0.40Pa
0.25 (2 / 8 ccm)		0.30Pa	0.30Pa	–

## Results and Discussion

Figures 1 show surface images of the  $r$ -plane oriented Cr<sub>2</sub>O<sub>3</sub> thin films grown at 580°C, 620°C, and 660°C of the  $T_S$  under the circumstances of 0.25, 1.0, and 2.0 of the introduced gas O<sub>2</sub>/Ar ratio, respectively. In figure 1(a),

approximately  $300 \times 300 \text{ nm}^2$  grains were observed with a deep holes of 20-30 nm in depth between grains. The grains were coalesced, where the steps with 1.5-2.0 nm in height were observed. Within one grain, meaning not coalesced grain, the unit step, approximately 0.35 nm, was observed. Increasing the  $T_S$ , the region of the holes expanded. The height difference at the coalesced position was 2-3 nm. However, the surface in one grain was quite smooth. In figure 1(c), grain size enlarged by the coalescence. Steps with the height of 1-1.5 nm were often observed on the surface. At  $660^\circ\text{C}$  as shown in figure 1(d), the trapezoid-like grains appeared with the deeper holes of 60-80 nm. Increasing oxygen partial pressure as shown in figure 1(e), the grain structure was same to that of figure 1(d), but the grain size somewhat developed.

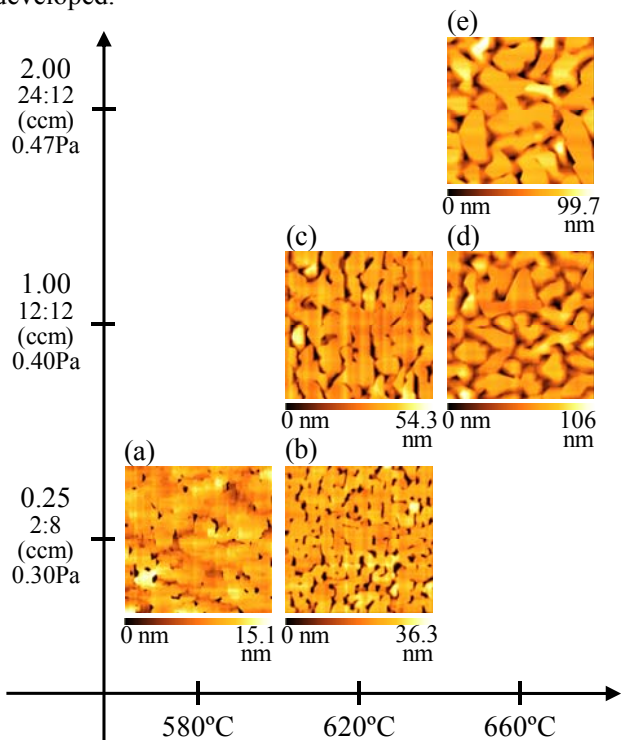


Fig.1 Surface images of  $\text{Cr}_2\text{O}_3$  thin films depending on the  $T_S$  and the atmosphere, introduced  $\text{O}_2/\text{Ar}$  ratio, during growth.

In Table 1, the surface roughness  $R_a$  is summarized from the picture shown in figures 1. Increasing the  $T_S$ , the  $R_a$  was also increased, indicating the surface became rougher. It is noted that the  $R_a$  was almost same at  $660^\circ\text{C}$  with different  $\text{O}_2/\text{Ar}$  ratio.

In all specimens, only  $r$ -plane related Bragg peaks appeared at the lower side form that of sapphire substrate. The full width at half maximum (FWHM) of rocking curve for  $\text{Cr}_2\text{O}_3(2-204)$  is summarized in Table 1. Increasing the the  $T_S$  and the  $\text{O}_2/\text{Ar}$  ratio, the FWHM was improved, indicating that the crystallinity was better. The surface became rough at the higher  $T_S$ , while the crystallinity was improved. From our previous results a relaxation started from the beginning, roughly 1 nm, of the film growth probably due to the lattice mismatch of 4.1%, where the two dimensional (2D) island grains grew. The correspondence of the lattice spacing of the film to

that of bulk  $\text{Cr}_2\text{O}_3$  was consistent with the relaxation. In the same manner, the grain-growth occurred at the higher  $T_S$ , which makes the film crystallinity better, but a rather three dimensional (3D) growth was involved.

Table 2 Summary of surface roughness  $R_a$  and full width at half maximum (FWHM) of rocking curve for  $\text{Cr}_2\text{O}_3(2-204)$  Bragg diffraction as the functions of the  $T_S$  and growth atmosphere during growth.

$\text{O}_2/\text{Ar}$ ratio	$T_S$ ( $^\circ\text{C}$ )	580	620	660
2.0 (24/12 ccm)	$R_a$ (nm)	–	–	13.7
	FWHM (degree)	–	–	0.350
1.0 (12/12 ccm)	$R_a$ (nm)	–	6.48	14.0
	FWHM (degree)	–	0.536	0.374
0.25 (2/8 ccm)	$R_a$ (nm)	1.56	4.50	–
	FWHM (degree)	0.540	0.458	–

## Conclusion

In order to achieve the high  $H_{\text{EB}}$  in the FM metals /  $r$ - $\text{Cr}_2\text{O}_3$  multilayer, the growth of the  $r$ -plane oriented  $\text{Cr}_2\text{O}_3$  thin films were investigated. The point is the FM order of spins of Cr ions at the  $r$ -surface, therefore the smooth surface of the film is required. The  $T_S$  was increased to get rid of the deep holes and to obtain the smooth surface. However the crystallinity was improved but the surface became rough probably due to the grain-growth and the introduction of the 3D growth. It is expected that some buffer layer is necessity to enhance the 2D growth by reducing the lattice mismatch.

## References

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