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Stress Effects $CoCr_2O_4$ Film on MgO and $MgAl_2O_4$ Grown by RF-Sputter Process

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Multiferroic $CoCr_2O_4$ film was deposited on MgO and $MgAl_2O_4$ substrates by the rf-sputtering process. The films were prepared at an RF-magnetron sputtering power of 50 W and a pressure of 10 mtorr (20 sccm in Ar), and at substrate temperatures of 550 °C. The crystal structure was determined to be a spinel (F*d-3m*) structure by means of X-ray diffraction (XRD) with Cu *K*¥á radiation. The thickness and morphology of the films were measured by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The magnetic properties were measured using a Superconducting Quantum Interference Device (SQIUD) magnetometer. While the ferrimagnetic transitions were observed at about 93 K, which was determined as the Néel temperature, the magnetic properties all show different behaviors. The differences between the magnetic properties can be explained by the stress effects between $CoCr_2O_4$ and the substrates of MgO and $MgAl_2O_4$.

Keywords : multiferroic, RF sputtering

1. Introduction

Multiferroic materials demonstrate the coexistence of ferromagnetic and ferroelectricity [1]. With multiferroic materials, an external electric and magnetic field can control magnetization and electric polarization, respectively. This means that magnetic and electric properties are strongly coupled together with spin-orbital-charge-lattice interaction. Multiferroic properties can be used in multifunctional devices, and a great deal of research has been carried out on multiferroic materials [2, 3]. Multiferroic $CoCr_2O_4$ materials have Co^{2+} ions on the A sites and Cr^{3+} on the B sites of the spinel structure. Ferroelectric transition has been observed in $CoCr_2O_4$ upon the transition to the spiral spin behavior of about 28 K [4, 5]. It has been suggested in the Lyons, Kaplan, Dwight, and Menyuk (LKDM) theory, and the local spin density approximation plus Hubbard U (LSDA + U) theory [6, 7], that these phenomena are caused by spin-orbital-charge-lattice coupling.

In this research, we have investigated the crystallographic and magnetic structure on the basis of the lattice mismatch effects on $CoCr_2O_4$ (a_0 = 8.33 Å) thin films on MgO (a_0 = 4.22 Å) and $MgAl_2O_4$ (a_0 = 8.08 Å) substrates [8] grown by RF-sputter [9]. We have measured crystallographic and microscopic properties of $CoCr_2O_4$ thin films on MgO and $MgAl_2O_4$ substrates using an x-ray diffractometer (XRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM) [10]. Magnetization measurements were carried out using a super conducting quantum interference device (SQUID) magnetometer system.

2. Experimental Procedure

$CoCr_2O_4$ powder was prepared by the solid-state reaction of a stoichiometry mixture of CoO (99.99%) and Cr_2O_3 (99.99%) powder at 1000 °C in air for 10 h. The $CoCr_2O_4$ powder was pressed into a pellet (2 inch diameter) and used as a target for RF-sputtering. Cleaned substrates were loaded in the central region of the substrate holder located 12 cm away from the target. The deposition conditions are summarized in Table 1.

The crystal structure was examined using an X-ray diffraction (XRD) with Cu-$K\alpha$ radiation at room temperature. The thin film thickness and morphology were measured by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Magnetization measurements were carried out using a super conducting quantum interference device (SQUID) magnetometer system.

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Table 1. Sputter condition of $CoCr_2O_4$ thin films.

Target	Single-phased $CoCr_2O_4$
Substrates	$MgAl_2O_4$ and MgO
Base Pressure	1.0×10^{-6} Torr
Working Pressure	10 m Torr
Substrate Temperature	550 °C
Deposition rf- Power	50 W
Deposition Time	3 h
Flow Gas	Ar 20 sccm

3. Results and Discussion

Fig. 1 shows the results of X-ray diffraction patterns for the $CoCr_2O_4/MgAl_2O_4$ and $CoCr_2O_4$/MgO thin films, at room temperature. For the lattice constants of the $CoCr_2O_4$ target, $a_0 = 8.33$ Å. According to X-ray diffraction analysis, $CoCr_2O_4$ thin films grew in the single phase and at (400) pre-orientation on each of the substrates. For the rocksalt MgO substrate, the lattice constants ($2a_0 = 8.44$ Å) are slightly larger than those of the $CoCr_2O_4$ target, while for the spinel $MgAl_2O_4$ substrate the lattice constants ($a_0 = 8.08$ Å) are slightly smaller than those of the $CoCr_2O_4$ target. For $CoCr_2O_4$ on the MgO substrate, the lattice constants ($a_0 = 8.32$ Å) are slightly smaller than those of the $CoCr_2O_4$ target ($a_0 = 8.33$ Å), while for $CoCr_2O_4$ on the $MgAl_2O_4$ substrate the lattice constants ($a_0 = 8.35$ Å) are slightly larger than those of the $CoCr_2O_4$ target. Therefore, as can be seen in Fig. 1, the XRD $\theta/2\theta$ spectra shows that 2θ degree of CCO(400) peak was larger than MgO(100), while it was smaller than $MgAl_2O_4$(100). The full width of half the maximum of the rocking curve of the (004) reflection of CCO on both MgO and $MgAl_2O_4$ substrates is below 0.03°. This means that both samples are well-oriented and have opposite mismatches.

The surface morphology and microstructures of the thin films are shown in Fig. 2. The morphology of film shows clear isolated grains and ellipse shapes. In each thin film, the root mean square (RMS) values and particle sizes of CCO on MgO thin film were 7.5 nm and 70 nm, respectively, while those for the CCO on $MgAl_2O_4$ thin film were 8.2 nm and 70-105 nm, respectively. CCO on MgO thin film grew uniformly, compared with CCO on $MgAl_2O_4$ thin film. From this result, it can therefore be concluded that uniformity is strongly related to lattice mismatches of substrates. The thicknesses of thin films

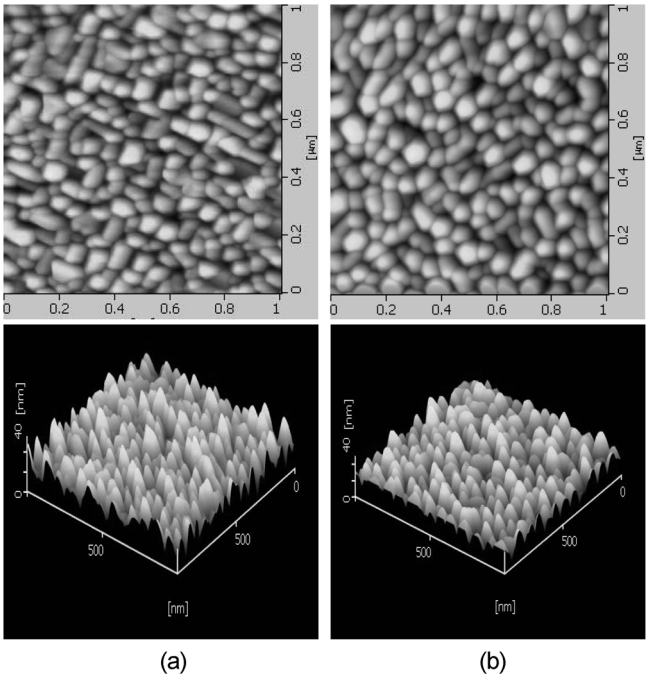

Fig. 2. AFM image of (a) $CoCr_2O_4/MgAl_2O_4$ thin film and (b) $CoCr_2O_4$/MgO thin film.

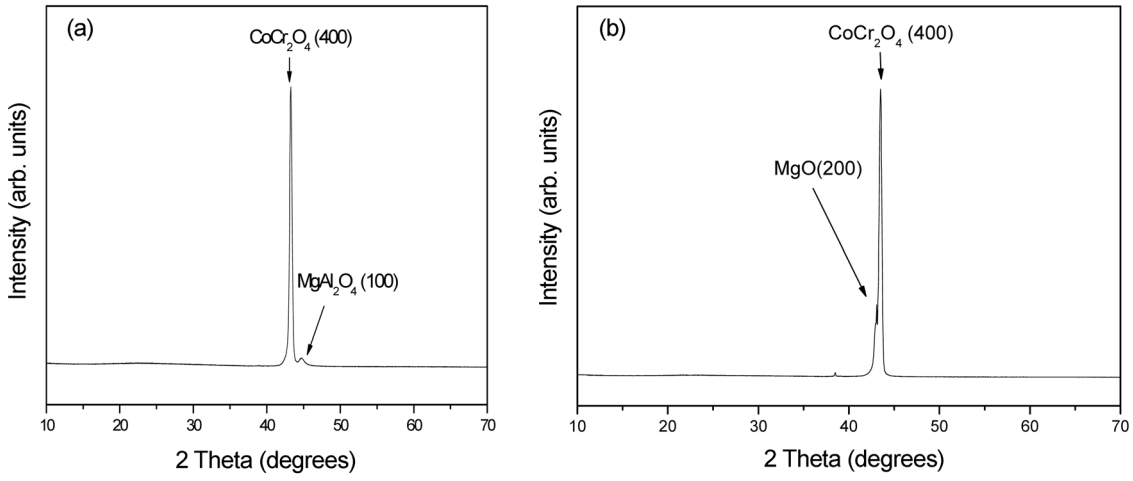

Fig. 1. X-ray diffraction patterns of (a) $CoCr_2O_4/MgAl_2O_4$ thin film and (b) $CoCr_2O_4$/MgO thin film.

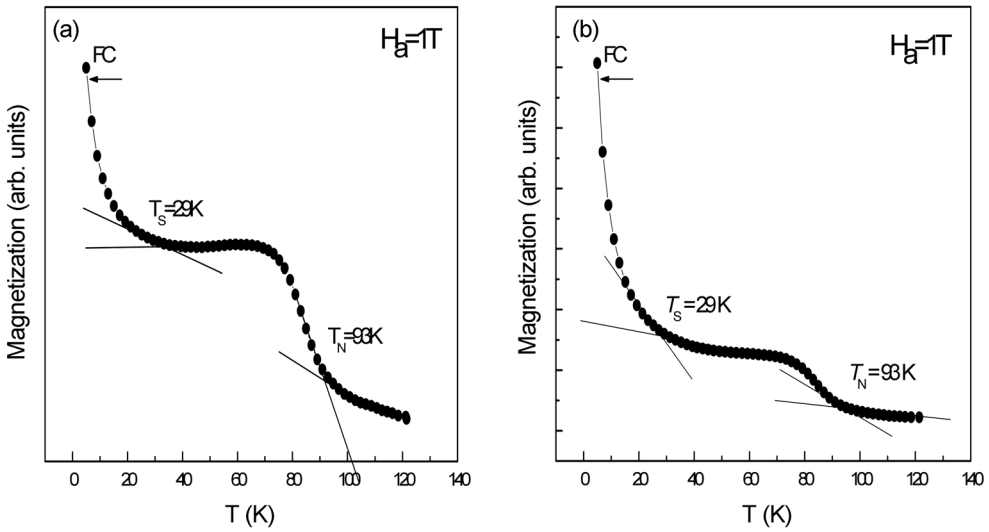

Fig. 3. Magnetization curves for (a) $CoCr_2O_4/MgAl_2O_4$ thin film and (b) $CoCr_2O_4$/MgO thin film at various temperatures with 1T applied fields by SQUID.

are about 400 nm by scanning electron microscopy (SEM).

Magnetization measurements were carried out using a super conducting quantum interference device (SQUID) magnetometer. In these measurements, the magnetic field (1T) was applied in the plane of the substrate. Fig. 3 shows magnetization curves for (a) $CoCr_2O_4/MgAl_2O_4$ thin film and (b) $CoCr_2O_4$/MgO thin film. According to Fig. 3, the ferrimagnetic transitions were observed at around 93 K, which was determined as the Néel temperature, and the spiral magnetic transition temperatures (T_S) were 29 K, while the T_S of the CCO target was 28.0 K. There are no sizeable changes in T_S between the bulk CCO and the thin films. With decreasing temperatures below T_S, the magnetization values of CCO on MgO change more significantly than those of CCO on $MgAl_2O_4$. Even though magnetic transition points are the same in all samples, they differ in magetization values below T_S due to the lattice mismatch. We suggest that the lattice mismatch between the CCO thin film and the substrates plays a very important role which could control the mechanical stress-mediated multiferroic coupling.

4. Conclusions

$CoCr_2O_4$ film was deposited on MgO and $MgAl_2O_4$ substrates by the RF-sputtering process. The films were prepared at an rf-magnetron sputtering power of 50W and a pressure of 10 mTorr (20 sccm in Ar), and at substrate temperatures of 550 °C. The lattice constants ($2a_0$ = 8.44 Å) of rocksalt MgO substrate are slightly larger than those of the $CoCr_2O_4$ (a_0 = 8.33 Å) target, otherwise the lattice constants (a_0 = 8.08 Å) of the spinel $MgAl_2O_4$ substrate are slightly smaller than those of the $CoCr_2O_4$ target. For each thin film, the root mean square (RMS) values and particle sizes for CCO on MgO thin film were 7.5 nm and 70 nm, respectively, while those for CCO on $MgAl_2O_4$ thin film were 8.2 nm and 70-105 nm, respectively. The ferrimagnetic transitions were observed at around 93 K, which was determined as the Néel temperature and the spiral magnetic transition temperatures (T_S) were 29 K, while the T_S of the CCO target was 28.0 K. With decreasing temperatures below T_S, the magnetization values of CCO on MgO changed more significantly than those for CCO on $MgAl_2O_4$. Even though magnetic transition points are the same in all samples, they differ in magetization values below T_S due to the lattice mismatch. The results of both magnetic properties can be explained by the stress effects of CCO between the films grown on the MgO substrate and the film grown on $MgAl_2O_4$. We suggest that the lattice mismatch between the CCO thin film and the substrates plays a very important role which could control the mechanical stress-mediated multiferroic coupling.

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