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Preparation and Magnetoresistance of Ordered Double-Perovskite Sr_2FeMoO_6 Thin Films

Hideaki Adachi, Yutaka Nakayama, Akihiro Odagawa,
Kentaro Setsune and Hiroshi Sakakima
Advanced Technology Research Laboratories,
Matsushita Electric Industrial Co., Ltd.,
3-4 Hikaridai, Seika, Kyoto 619-0237, Japan
Fax: 81-774-98-2585, e-mail: adachi@crl.mei.co.jp

Thin film formation of ordered double-perovskite Sr_2FeMoO_6 has been investigated using sputtering technique with Sr-Fe-Mo-O targets of different oxygen content. It was found that the restricted reduced-oxygen atmosphere was suitable for the growth of ordered double-perovskite structure. Using the appropriate sputtering target with reduced oxygen, double-perovskite Sr_2FeMoO_6 thin films could be obtained both *in situ* with substrates heated at 800°C and by post annealing of amorphous films at 950°C in argon atmosphere. The films on $SrTiO_3$ single-crystal substrates grew epitaxially and showed clear superstructural XRD peaks caused by ordering of Fe and Mo ions along the <111> axis. The epitaxial Sr_2FeMoO_6 films on $SrTiO_3$ single crystals exhibited less magnetoresistance properties at R.T., whereas the polycrystalline films on YSZ ceramics exhibited significant magnetoresistance.
Key words: double perovskite, Sr_2FeMoO_6 , thin film, sputter, magnetoresistance

1. INTRODUCTION

Tunneling magnetoresistance (TMR) devices[1] are one of the promising candidates for future sensing heads of high-density magnetic storage and/or for magnetic random access memory. Although the practical studies have been developed using conventional magnetic metals (Co,Fe,Ni) for magnetic electrodes of TMR[2], half-metallic ferro- or ferri-magnetics which possess 100% spin polarization have attracted much attention[3] for that electrode materials. Considerable high TMR are expected for half metals from the relation $TMR=2P^2/(1-P^2)$ [P: spin polarization]. Many half metallic materials are predicted and verified in the compounds with transition-metal oxides such as manganites $(La,A)MnO_3$[4]. Recently, ferrimagnetic Sr_2FeMoO_6 has been also found to be a half metal with higher T_C of 450 K than manganites[5]. The structure is regularly ordered double-perovskite, where A-site is Sr ion and B-site Fe and Mo ions arrange in the NaCl structure. Thin films of this material have also been grown for the purpose of device application as well as basic research[6] [7].

The key point for the preparation of half metallic Sr_2FeMoO_6 is how we can make ordered structure in B-site Fe and Mo ions. Recently we have investigated the phase formation of ordered structure in Sr_2FeMoO_6 thin films using sputtering technique. Here we report the thin-film preparation of double perovskite Sr_2FeMoO_6 and their properties such as magnetoresistance.

2. FILM PREPARATION

2.1 Growth conditions

Sr_2FeMoO_6 thin films were fabricated using rf-planar magnetron sputtering with mixed compound targets of Sr-Fe-Mo-O. Substrates used were $SrTiO_3$ single crystals and polycrystalline yttrium-stabilized-zirconia (YSZ) ceramics. Especially, (111) plane of $SrTiO_3$ was mostly used for substrates since the Fe/Mo ordering of the film was easily evaluated from x-ray diffraction peaks in this substrate orientation. Sputtering was carried out in a pure argon atmosphere of about 0.6 Pa using the various targets with different oxygen contents. Input rf power was 150 W for 3-inch-diameter target and substrates were heated in the range from room temperature to 850°C during the deposition.

Figure 1 displays the crystalline structure of the films grown *in situ* at 800°C from different sputtering Sr_2FeMoO_X targets with a variety of oxygen content. It was found that the simple perovskite structure with disordered B-site ions was dominantly obtained from the most targets. Restricted reducing atmosphere was considered to be suitable for the arrangement of B-site

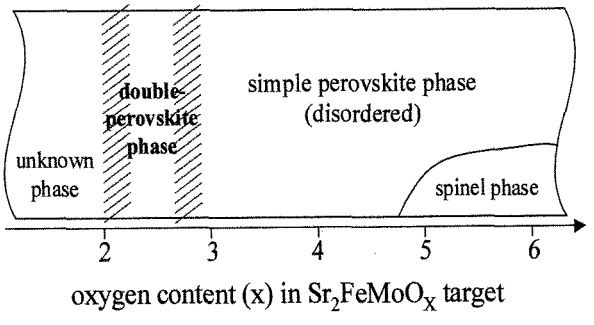

Fig. 1. Crystalline structure of the Sr-Fe-Mo-O films grown *in situ* at 800°C from Sr_2FeMoO_X targets.

Fe and Mo ions, which resulted in the formation of ordered double-perovskite structure. Similar to the case of *in situ* preparation, post-annealing method could also make ordered double-perovskite structure in thin films. The amorphous films deposited at room temperature from the same restricted oxidizing target were heated in 1 atm argon flow at 950°C for 30 min, and ordered double-perovskite structure was grown in a solid phase. The amorphous films deposited from the other oxidized targets were found not to change into ordered structure but simple perovskite one.

2.2 Structural properties

Figure 2 shows the x-ray diffraction pattern of the Sr_2FeMoO_6 film grown on (111) surface of $SrTiO_3$ by post-annealing method. In addition to the simple perovskite peaks (a a a) [a: even], extra peaks (b b b) [b: odd] caused by the ordered structure are clearly seen, which indicates the successful arrangement of Fe and Mo ions. By employing x-ray reciprocal space mapping measurement, planar alignment of double-perovskite Sr_2FeMoO_6 lattice was confirmed, indicating the solid-phase epitaxy. For other $SrTiO_3$ substrates with different surface orientation, epitaxial growth of the double-perovskite structure was also found by measuring ordered peaks using the reciprocal mapping. Figure 3 shows the x-ray ϕ scan of ordered {511} reflections for Sr_2FeMoO_6 film grown on $SrTiO_3$ (100) substrate. Fourfold in-plane symmetry was clearly recognized with peak of every 90-degrees ϕ angle. For the film grown on YSZ ceramic substrates, polycrystalline Sr_2FeMoO_6 films were obtained.

Figure 4 displays the atomic force microscope (AFM) image of Sr_2FeMoO_6 surface on (111) $SrTiO_3$. Grain structure of about 2000Å in diameter was observed in the surface. The rough textured structure was seen and the arithmetical-mean-deviation (Ra) of the surface is as large as 40nm in this film, which may be due to the higher processing temperature than the other perovskite oxides. Figure 5 is the cross-

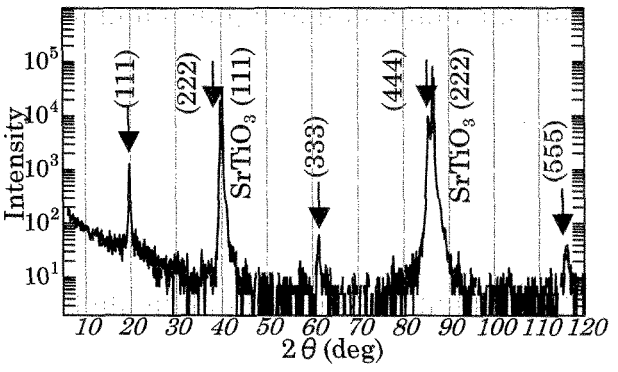

Fig. 2. Standard θ-2θ x-ray diffraction pattern for Sr_2FeMoO_6 thin film grown on $SrTiO_3$ (111).

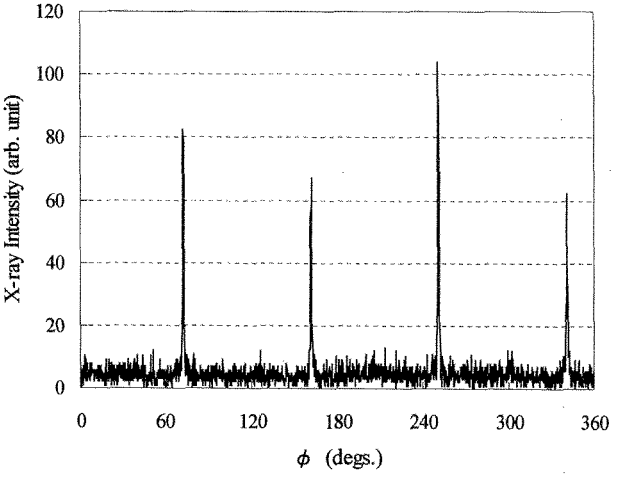

Fig. 3. X-ray ϕ scan of the Sr_2FeMoO_6 {511} reflections of the thin film grown on $SrTiO_3$ (100).

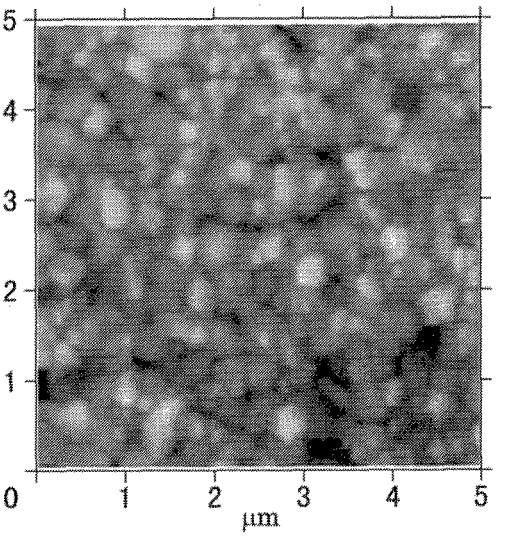

Fig. 4. AFM image of Sr_2FeMoO_6 film surface grown on $SrTiO_3$ (111).

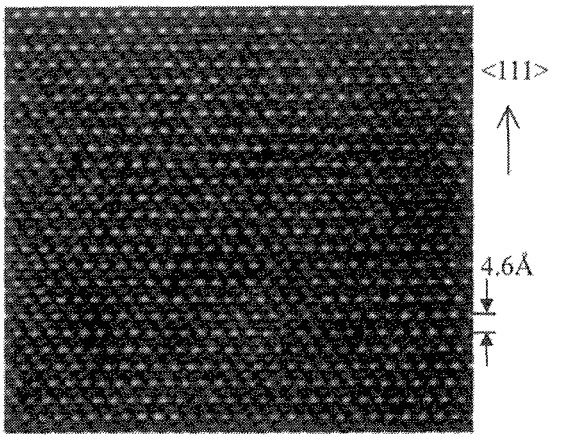

Fig. 5. Cross-sectional transmission electron microscopy image for epitaxial Sr_2FeMoO_6 thin film grown on $SrTiO_3$ (111).

sectional TEM image of (111) Sr_2FeMoO_6 film. Alternate layering structure with a period of 4.6Å was seen along <111> direction, indicating the ordered arrangement of B-site Fe and Mo ions.

3. ELECTRIC AND MAGNETIC PROPERTIES

Electric properties of Sr_2FeMoO_6 films were measured using a dc four-probe method with Au electrodes put on the film surface. Figure 6 shows the temperature dependence of the resistivity of as-prepared double perovskite Sr_2FeMoO_6 thin films on $SrTiO_3$ (111) and those after weak oxidation. The as-prepared film exhibited metallic behavior (Fig.6 (a)) with the relatively low resistivity of less than 4mΩcm. The film resisrivity was easily affected by the oxygen annealing at a low temperature of 300°C for 1h and 2h as shown in Fig.6 (b) and (c), respectively. Such weak oxidation even made thin films higher resistivity and more semiconductive behavior.

Under the magnetic field of 5 T, the resisrivity of the films decreased as shown in the figure. The variation of the film resistivity against the field increases as the decrease of temperature. The magnetoresistance (MR) properties of Sr_2FeMoO_6 thin films at different temperature were shown in Fig.7. The MR at 10 K is 5 times larger than that at 250 K, maybe due to the increase of spin polarization in lower temperature. The MR for the weakly oxidized films increased slightly (50% larger) although the film resistivity became two-order higher. The properties of the films did not show considerable differences among the any planes of $SrTiO_3$ substrates.

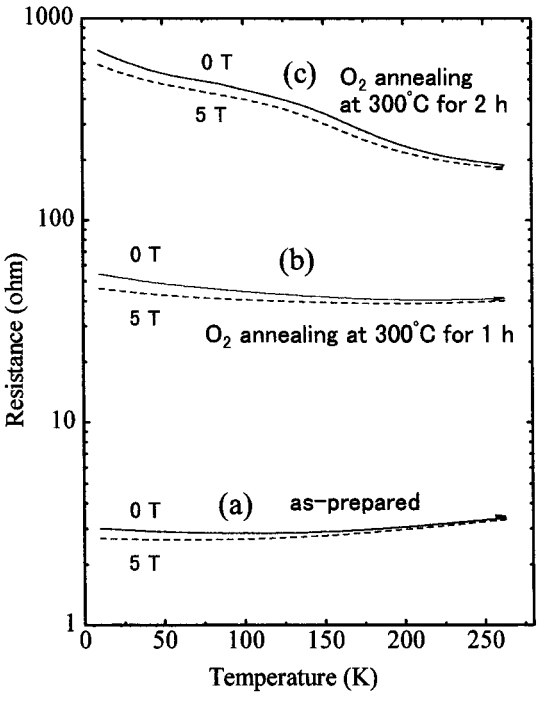

Fig. 6. Temperature dependence of the resistivity for the Sr_2FeMoO_6 thin film of as-prepared (a) and weakly oxygen annealed (b) (c) grown on $SrTiO_3$ (111).

At room temperature, the film exhibits ferromagnetic properties. Figure 8 shows the magnetization hysteresis curve of Sr_2FeMoO_6 film grown on $SrTiO_3$ (111) measured by a vibrating sample magnetometer. The magnetization at 5 kOe reaches 1.3 μ_B/f.u., which is lower than that of the ceramics (2.2 μ_B/f.u.) at R.T, although the magnetization of the film is not saturated yet. The magnetoresistance properties R.T. for the films on different substrates are shown in Fig.9. The epitaxial Sr_2FeMoO_6 film on $SrTiO_3$ substrate shows small MR ratio (<0.02%), whereas the polycrystalline film on YSZ exhibited relatively large MR ration of 0.7% under the small magnetic field of 500 Oe, which is compatible to the maximum low-field MR value for manganites $(La,Sr)MnO_3$ film at R.T.[8] The larger MR in polycrystalline film than epitaxial one is considered to be caused by intergrain nature such as intergrain tunneling and/or intergrain scattering.

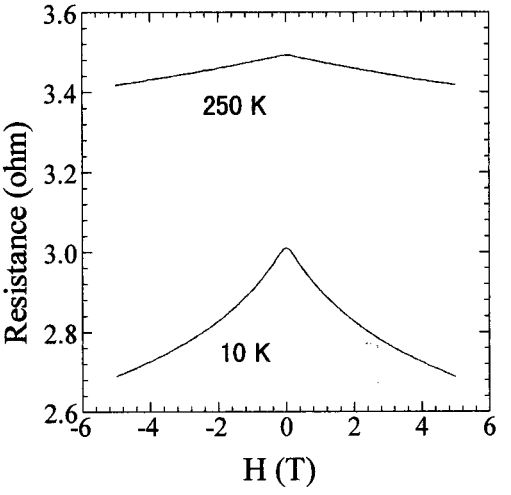

Fig. 7. Magnetoresistance for epitaxial Sr_2FeMoO_6 thin film on $SrTiO_3$ (111) at 10 K and 250 K.

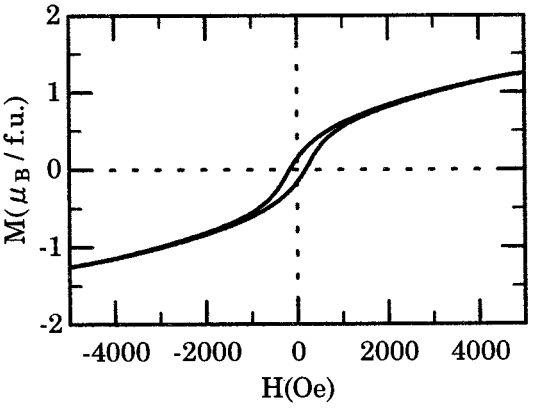

Fig. 8. Magnetization hysteresis curve for (111) Sr_2FeMoO_6 thin film measured at room temperature.

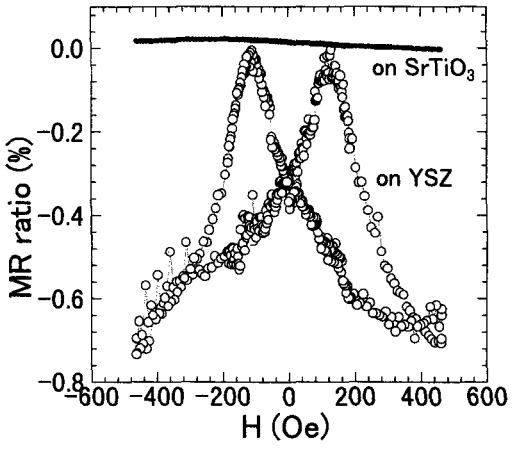

Fig. 9. Magnetoresistance of Sr_2FeMoO_6 films grown on $SrTiO_3$ and YSZ substrates.

4. SUMMARY

Thin films of ordered double-perovskite Sr_2FeMoO_6 has been prepared by sputtering technique with the restricted oxidizing target. Oxygen content was found to severely affect the formation of sputtered film structure. Using the appropriately reduced target, double-perovskite Sr_2FeMoO_6 thin films could be obtained both *in situ* with substrates heated at 800°C and by post annealing of amorphous films at 950°C in argon atmosphere. The films on $SrTiO_3$ single-crystal substrates grew epitaxially and showed clear superstructural XRD peaks caused by ordering of Fe and Mo ions along the <111> axis. The epitaxial Sr_2FeMoO_6 films on $SrTiO_3$ single crystals exhibited less magnetoresistance properties at R.T., whereas the polycrystalline films on YSZ ceramics exhibited significant magnetoresistance.

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