

Growth and properties of high-Curie-temperature $\text{Sr}_2\text{CrReO}_6$ thin films

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Thin films of ordered double-perovskite $\text{Sr}_2\text{CrReO}_6$ have been grown epitaxially onto SrTiO_3 substrates by sputtering, and their microstructural, electrical, and magnetic properties are investigated. It is found that a wide growth-temperature range of at least 700–800 °C can yield epitaxial films with superior magnetic properties and atomically flat surfaces. These films exhibit Curie temperatures T_c of up to 620 K, and saturation magnetizations M_s of $0.9\mu_B$ /formula unit (f.u.), which is comparable to the predicted value of $1\mu_B$ /f.u. for the fully ordered half-metallic material. Owing to the wide temperature window for growth of high-quality films, the surface morphology and coercivity of $\text{Sr}_2\text{CrReO}_6$ films are highly controllable, which is favorable for fabrication of magnetic tunnel junctions. © 2004 American Institute of Physics.

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Half-metallic compounds, i.e., compounds with only one spin channel present at the Fermi energy, are interesting for their potential applications in spin electronics. Mixed-valence manganese oxides have been identified to exhibit half-metallicity at low temperatures,^{1,2} but the spin polarization is strongly reduced at room temperature due to their low Curie temperatures below 370 K. It has been reported by Kobayashi *et al.*³ that $\text{Sr}_2\text{FeMoO}_6$ with an ordered double-perovskite structure exhibits high spin polarization. Its high Curie temperature, $T_c=420$ K, makes it a promising candidate for use at room temperature. Following this work, various investigations^{4–7} on $\text{Sr}_2\text{FeMoO}_6$, and related compounds of the ordered double-perovskite family, have been conducted to explore optimized properties. Most recently, $\text{Sr}_2\text{CrReO}_6$, a compound of the same family, was shown to have the highest Curie temperature of 635 K among perovskite oxides.⁸ In the simple ionic picture, Cr^{3+} ($3d^3, S=3/2$) ions in B sites are antiferromagnetically coupled with neighboring Re^{5+} ($5d^2, S=1$) ions in B' sites, and thus a saturation magnetization M_s of $1\mu_B$ /formula unit (f.u.) has been predicted⁸ for an ideal picture of complete B/B' (Cr/Re) ordering. As confirmed in the previous studies^{9–11} on $\text{Sr}_2\text{FeMoO}_6$, the existence of antisite defects at the B/B' sites would lead to a reduction in the M_s values, which presumably destroys the half-metallic nature of the material. To take advantage of the half-metallic nature leading to a full spin polarization of itinerant carriers in room-temperature spin transport examinations, the controllable preparation of high-quality epitaxial films of ordered double-perovskite ferromagnets, showing both a high T_c and full magnetization, is very important. We report on the thin-film growth of $\text{Sr}_2\text{CrReO}_6$ with high M_s and high T_c .

The preparation of high-quality thin films of ordered double-perovskite ferromagnets has been often hindered by several problems, including reduced B -site ordering and the inclusion of the impurity phases or the outgrowth.^{12,13} This difficulty is possibly related to the narrow and severe growth conditions of a reducing (low oxygen pressure) atmosphere and a high temperature above 800 °C. In fact, the M_s

values of thin films of $\text{Sr}_2\text{FeMoO}_6$ grown on SrTiO_3 , with a relatively large (1%) lattice mismatch to bulk $\text{Sr}_2\text{FeMoO}_6$, have been observed to be appreciably lower^{14–16} than the ideal values of $4\mu_B$ /f.u. Recently, we have reported¹⁷ that sputter deposition in an $\text{Ar}+\text{H}_2$ gas atmosphere on completely lattice-matched (lattice mismatch less than 0.1%) underlayers (substrates) of $\text{Ba}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ can produce $\text{Sr}_2\text{FeMoO}_6$ thin films with a reasonably high M_s value of $3.7\text{--}3.8\mu_B$ /f.u. and a high T_c of 380–390 K. It has been speculated that coherent growth of $\text{Sr}_2\text{FeMoO}_6$ films on completely lattice-matched underlayers could prevent the formation of defects (including antisite defects), which are prominent during the strain relaxation process for growth of the lattice-mismatched $\text{Sr}_2\text{FeMoO}_6/\text{SrTiO}_3$ system. In this letter, we report on the epitaxial growth and characterization of $\text{Sr}_2\text{CrReO}_6$ films by sputtering in an $\text{Ar}+\text{H}_2$ gas atmosphere. We will show that these sputtered $\text{Sr}_2\text{CrReO}_6$ thin films exhibit well-defined surface and magnetic properties.

$\text{Sr}_2\text{CrReO}_6$ thin films were deposited using a magnetron sputtering technique from a target with stoichiometric composition. The substrate used was polished SrTiO_3 (001)- and (111)-single crystals, of which the lattice mismatch is less than 0.1% to the half of the a axis ($0.3903\text{ nm}=7.806\text{ nm}/2$) of $\text{Sr}_2\text{CrReO}_6$. The $\text{Sr}_2\text{CrReO}_6$ films were grown at a temperature of 700–800 °C in a 76 mTorr $\text{Ar}+0.5\%\text{H}_2$ sputtering gas atmosphere with thicknesses of 100–200 nm. The orientation, phase purity, and lattice spacing of the films were examined by x-ray diffraction (XRD). The surface morphology and roughness of the films were characterized by atomic force microscopy (AFM). Using the standard four-point technique, the electrical resistivity was measured as a function of temperature. The magnetization measurements were performed using a vibrating sample magnetometer in the parallel (H in the film plane) geometry.

Figure 1 shows diffraction patterns for the $\text{Sr}_2\text{CrReO}_6$ films on (a) (001) and (b) (111) SrTiO_3 , indicating that both films grow epitaxially with the same orientation as those of the substrates. The logarithmic plot indicates a high phase purity of the films with a double-perovskite structure. The lattice spacing calculated from the XRD data for both (001)- and (111)- $\text{Sr}_2\text{CrReO}_6$ film was $0.7834\text{--}0.7842\text{ nm}$, which is comparable to, or slightly (0.2%–0.3%) larger than, the bulk

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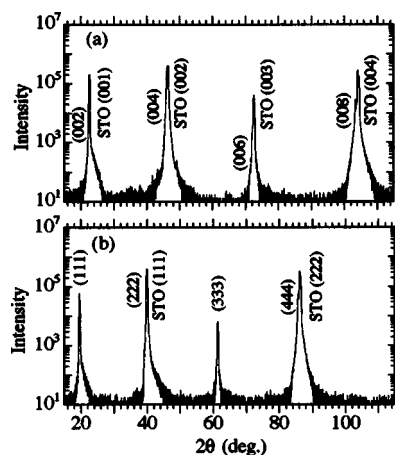


FIG. 1. X-ray diffraction patterns from $\text{Sr}_2\text{CrReO}_6$ thin films on (a) (001) SrTiO_3 and (b) (111) SrTiO_3 substrates.

c-axis lattice spacing of 0.7820 nm. For $\text{Sr}_2\text{CrReO}_6$ films on (111) SrTiO_3 , significant superlattice peaks, namely (111) and (333), can be observed, which indicates a high degree of Cr/Re ordering among the *B/B'* sites.

For both (001)- and (111)-oriented $\text{Sr}_2\text{CrReO}_6$ films, the microstructural, electrical, and magnetic characterizations were performed. Although these properties of the films show some dependence on the film orientations, the (001) and (111) films simultaneously grown in the same run showed very similar properties. Therefore, hereafter, we will concentrate on the results for (001)-oriented $\text{Sr}_2\text{CrReO}_6$ films. Typical temperature dependences of resistivity and magnetization for the $\text{Sr}_2\text{CrReO}_6$ films are presented in Fig. 2. The resistivity, as shown in the left panel in Fig. 2, shows a nearly flat temperature dependence in the range between 150 and 300 K, and a slight upturn is visible below 150 K. The room-temperature resistivity value is around 1 m Ω cm, which is about one order smaller than that⁸ of the bulk polycrystalline material. As seen in the right panel in Fig. 2, the ferromagnetic Curie temperature is around 620 K, which is slightly lower than the Curie temperature of 635 K for the bulk material. The magnetization value at a magnetic field of 1 T, which almost corresponds to the saturation magnetization M_s value in our $\text{Sr}_2\text{CrReO}_6$ films, is $0.9\mu_B/\text{f.u.}$ This value is close to the predicted half-metallic value of $1\mu_B/\text{f.u.}$ As far as the T_c and M_s values of the films prepared in this study are concerned, these values are less sensitive to the growth temperature.

Since future applications to magnetic tunnel junctions require a flat film surface and a proper coercive field H_c , we have examined surface morphology and magnetization hys-

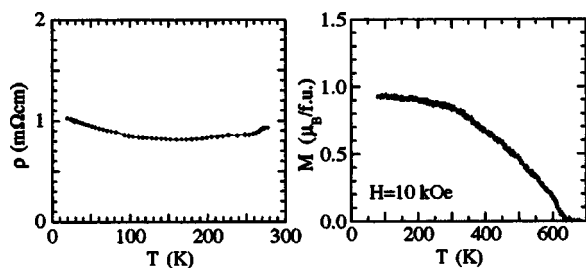


FIG. 2. The temperature dependence of resistivity ρ (left panel) and magnetization M (right panel) for (001)-oriented $\text{Sr}_2\text{CrReO}_6$ thin film. Magnetization was measured at a magnetic field $H=10$ kOe.

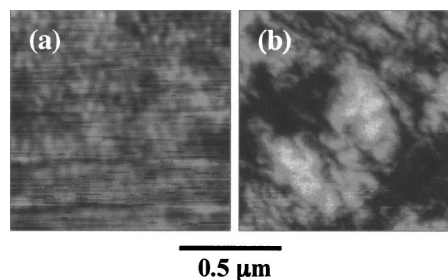


FIG. 3. AFM images for (001)-oriented $\text{Sr}_2\text{CrReO}_6$ thin films. (a) Film A grown at a substrate temperature $T_s=700$ K, and (b) Film B grown at $T_s=800$ K.

teresis for several $\text{Sr}_2\text{CrReO}_6$ films grown at different substrate temperatures. The surface morphology and surface roughness were found to depend on the substrate temperature as expected. Figure 3 shows AFM images for films grown at substrate temperatures T_s of (a) 700 $^\circ\text{C}$, and (b) 800 $^\circ\text{C}$. Film A ($T_s=700$ $^\circ\text{C}$), as shown in Fig. 3(a), has an average grain (or domain) size of about 50 nm, while film B, as shown in Fig. 3(b), grown at a higher substrate temperature T_s of 800 $^\circ\text{C}$ possesses grain (or domain) sizes of about 300–500 nm. The surface roughness (a rms) over the area of $1.5 \times 1.5 \mu\text{m}^2$ (shown in Fig. 3) is 0.4 and 1.2 nm for films A and B, respectively. It should be noted that AFM scans over a wider area of $10 \times 10 \mu\text{m}^2$ (not shown) have detected a surface roughness (rms) as small as 0.5 and 1.7 nm for film A and film B, respectively. This indicates excellent uniformity of the film surface over a wide area, which is the same order as those of magnetic tunnel junctions fabricated using conventional photolithography.

The corresponding magnetization loops for films A and B are shown in Fig. 4. Film A, as shown in Fig. 4(a), exhibits a distinct hysteresis loop with a large coercivity H_c of 3 kOe at 77 K and 1 kOe at 300 K. For the bulk polycrystalline material, a very large coercivity of 1.5 T at 4.2 K has been reported,⁸ which suggests a highly anisotropic nature for the magnetic materials. In contrast, film B, as shown in Fig. 4(b), shows a small hysteresis loop with H_c of 0.3 kOe at 77 K and 0.1 kOe at 300 K. At present, the detailed origins of the large difference in the hysteresis loop between the two films is unclear, but is at least in part related to their microstructures, as detected by AFM. It is also to be noted that both

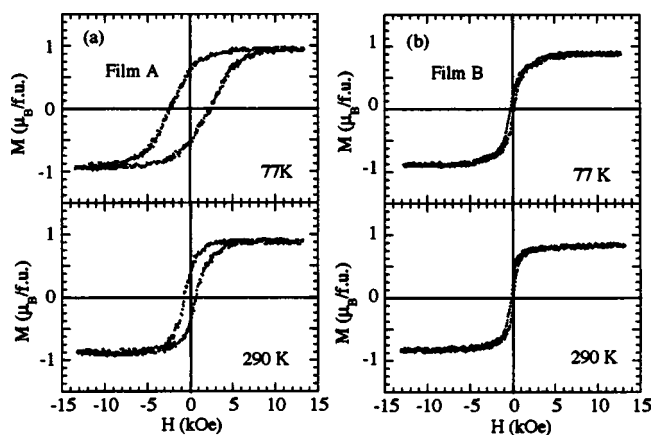


FIG. 4. Magnetization vs magnetic field loops for (001)-oriented $\text{Sr}_2\text{CrReO}_6$ thin films. (a) Film A grown at a substrate temperature $T_s=700$ K, and (b) Film B grown at $T_s=800$ K. The upper and lower panels are data measured at 77 and 290 K, respectively.

films show a magnetization larger than $0.8\mu_B/\text{f.u.}$, even though they were grown at different substrate temperatures.

Previous investigations^{14–16} on thin films of ordered double-perovskite $\text{Sr}_2\text{FeMoO}_6$ have shown that epitaxial films with superior properties can be prepared in a very narrow window of the temperature and oxygen pressure. In our study,¹⁷ by using sputter deposition in an $\text{Ar}+\text{H}_2$ gas atmosphere, the temperature window for the growth of $\text{Sr}_2\text{FeMoO}_6$ films with M_s larger than $3.5\mu_B/\text{f.u.}$ is as narrow as 800–830 °C. Therefore, control over the surface morphology and related coercivity by the choice of growth temperature is almost impossible for the $\text{Sr}_2\text{FeMoO}_6$ films. In the case of $\text{Sr}_2\text{CrReO}_6$ films, however, we found that at least in the temperature range of 700–800 °C, films can be prepared with M_s values comparable to the half-metallic value. Hence, while preserving a possible half-metallic character of the films, control over the surface morphology and related coercivity is possible.

In summary, we have succeeded in sputter deposition of $\text{Sr}_2\text{CrReO}_6$ epitaxial thin films having high T_c and high M_s comparable to the half-metallic value. It was shown that advantages of the $\text{Sr}_2\text{CrReO}_6$ system compared to the $\text{Sr}_2\text{FeMoO}_6$ system are not only high- T_c values, but also the ability for the growth of high-quality epitaxial films in a wide window of growth temperature range. We have also demonstrated that the coercivity of $\text{Sr}_2\text{CrReO}_6$ films can be controlled by about ten times (0.3–3 kOe at 77 K). These epitaxial films of $\text{Sr}_2\text{CrReO}_6$ are promising candidates to elucidate the intrinsic nature of the half-metallic ordered double-perovskite materials and also for the construction of multilayer tunneling devices.

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