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Pulsed-laser-deposited epitaxial Sr_2FeMoO_{6-y} thin films: Positive and negative magnetoresistance regimes

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Epitaxial thin films of ordered double-perovskite Sr_2FeMoO_{6-y} are deposited on (001) $SrTiO_3$ substrates by pulsed-laser deposition using a two step growth process. Selection of growth conditions is found to lead to either highly conductive metallic thin films (residual resistivity of about 1 $\mu\Omega$ cm) or semiconducting films. The metallic films show a positive magnetoresistance (MR) as high as 35%, while the semiconducting films show a negative MR of -3%, at a temperature of 5 K and a field of 8 T. © *1999 American Institute of Physics.* [S0003-6951(99)03024-7]

Research on the magnetoresistance (MR) effect in magnetic multilayers and oxides is currently a very active field because of the scientific interest as well as possible technological applications. A large negative MR has been reported in artificial metallic thin film multilayers,[1,2] ''half-metallic ferromagnetic'' oxides such as perovskite manganites,[3–6] pyrochlore manganites,[7] magnetites,[8,9] and in spin-polarized tunneling configurations.[10–12] In contrast, a large positive MR effect has been recently observed in several layered structures.[13–16]

Most recently, interest has been emerging in the magnetotransport properties of the ordered double perovskite Sr_2FeMoO_6 and related half-metallic ferromagnets.[17] It has been known that Sr_2FeMoO_6 has a double perovskite structure with ionic ordering on the transition metal sites, and is metallic with ferromagnetic (or ferrimagnetic) Curie temperature of 410–450 K.[18,19] Polycrystalline bulk samples of this ordered double perovskite exhibit large negative MR effect due to grain-boundary tunneling, which persists well above the room temperature.[17] This suggests that the double perovskite family of materials holds promise for utilization as electrodes for spin valve and magnetic tunnel junction devices. In this letter, we report on the growth of epitaxial thin films of Sr_2FeMoO_6 by pulsed laser deposition (PLD), and study of their magnetic and transport properties. Interestingly, we observe occurrence of physical states in the films which show either a large positive or a negative MR.

Sr_2FeMoO_{6-y} thin films were grown under vacuum on $SrTiO_3$ (001) by the pulsed laser deposition technique. Typical deposition conditions are as follows: base pressure of 5×10^{-7} Torr, pressure during deposition of 1.5×10^{-6} Torr, substrate temperature of 600–850 °C, laser energy density of 2.0 J/cm^2, and deposition rate of 20 nm/min. A perovskite phase grows epitaxially on $SrTiO_3$(001) under vacuum with a pressure less than 10^{-5} Torr over a wide substrate temperature range of 600–850 °C. However, the behavior of the out-of-plane lattice constant and the temperature-dependent resistivity is highly dependent on the substrate temperature. The general features of films grown at lower temperatures are, a clean single phase with large lattice constants and high resistivity values with a semiconducting-like temperature dependence. Films directly grown at higher temperatures are characterized by inclusion of a slight amount of impurity phases, small lattice constants, and relatively low resistivity values. Therefore, we adopted a two step process, that is, first a very thin layer of 5 nm is deposited at 600 °C, and then a thicker layer is deposited at a higher temperature of 800–850 °C.

The typical x-ray diffraction patterns (on expanded scale) for thin films grown using the two step process are shown in Fig. 1. The temperature used to deposit the thicker second layer is 800 °C for film A and 850 °C for film B. The out-of-plane lattice constants were determined to be 0.7933 and 0.7895 nm for films A and B, respectively. The observed large difference of the lattice constants could be ascribed to the change in the disordering on the Fe and Mo sublattices and/or a change in the oxygen concentration.

In Fig. 2, we show a comparison of the temperature-dependent resistivity $\rho(T)$ for films A and B. While film A has much higher resistivity and its temperature dependence is characteristic of a semiconductor, film B exhibits good metallic behavior. The residual resistivity of film B is as low as 1 $\mu\Omega$ cm which is about three orders magnitude lower than that of film A.

The magnetic-field dependent MR and magnetization M at 5 K are shown in Figs. 3(a) and 3(b), for the films A and B, respectively. For film A, the sign of MR measured at 5 K is negative, and the magnitude of MR gradually increases reaching a value of -3% in a field of 8 T. The M–H curve for film A exhibits an initial rise in M up to a field of 0.5 T, and gradual increase above 1 T, which is characterized by incomplete magnetic saturation. For films of type A, the shape of MR–H corresponds to the shape of the M–H curve at moderate and high fields, indicating that the negative MR has some correlation with the magnetization or spins in the resistive film.

For the conductive film B [Fig. 3(b)] the sign of MR is positive and the magnitude of positive MR measured at 5 K

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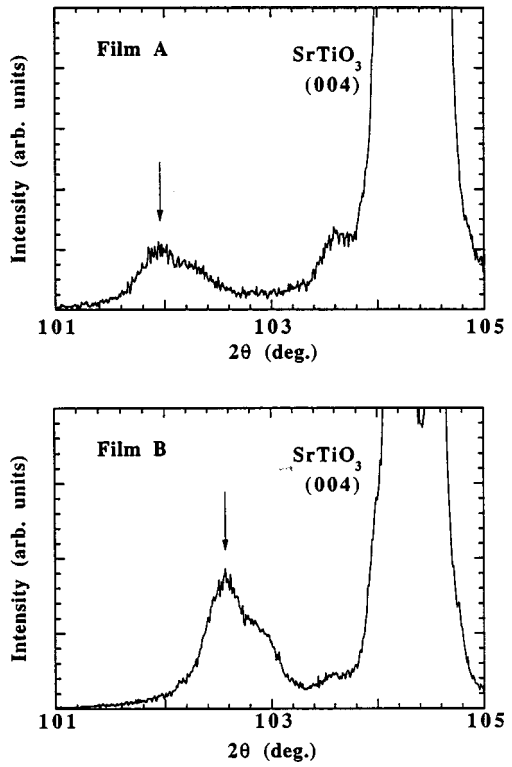

FIG. 1. X-ray diffraction patterns for the Sr_2FeMoO_{6-y} thin films grown using a two step process (see in the text). The initial layer of 5 nm was grown at 600 °C for all films. The subsequent layer of about 300 nm was deposited at 800 (film A) and 850 °C (film B).

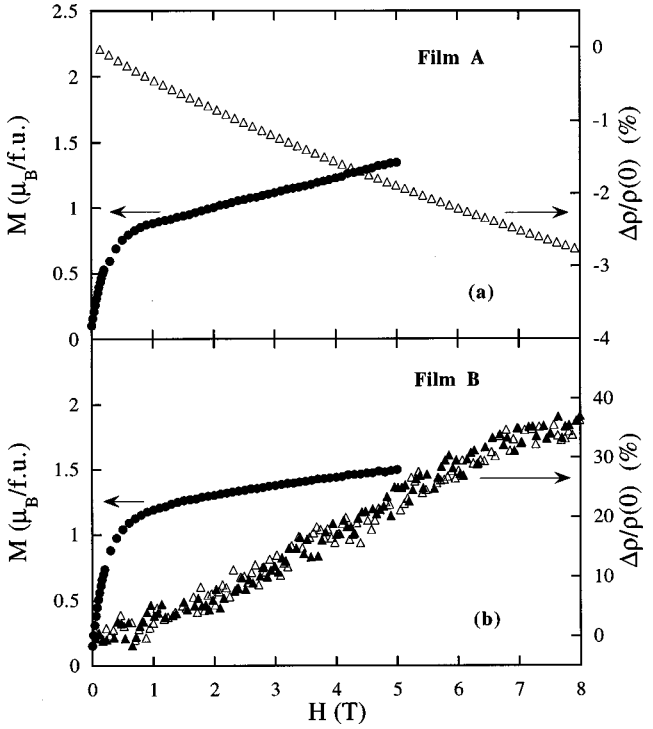

FIG. 3. The field dependences of magnetoresistance and magnetization for the Sr_2FeMoO_{6-y} thin films of types A and B. The closed and open symbols represent data for increasing and decreasing fields, respectively.

increases nearly linearly with the increase in the magnetic field, attaining a value of 35% in a field of 8 T. It can also be seen that the MR is not saturated even at 8 T and that the MR–H curve displays no hysteresis. The field dependence of M for the film B is qualitatively similar to that of the film A. The H dependence of positive MR however is quite different from the H dependence of M, implying that they arise from different causes, and that the positive MR has no direct correlation with the magnetization of the conductive film. This possibly points to the significance of the interface magnetism in the mechanism of positive MR, as discussed in the literature.[13–15]

In Fig. 4 we compare the microstructural and compositional features of films A and B as revealed by transmission electron microscopy (TEM). The microstructure of film A exhibits a spray of nanoclusters (size ~10–15 nm, with some larger ones) superimposed on a uniform background. The clusters were found to be epitaxial with the matrix. In film B [Fig. 4(b)], the clusters seem to have grown substantially to a size of over 100 nm. Energy dispersive x-ray

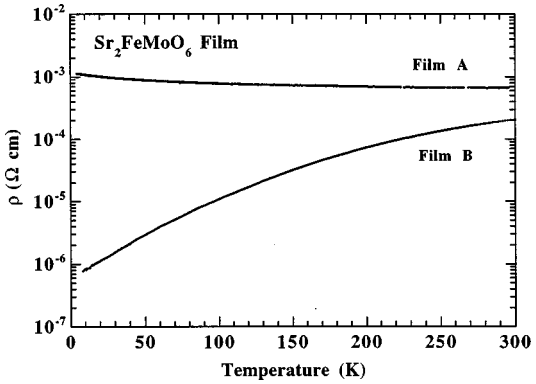

FIG. 2. The temperature dependence of resistivity ρ for Sr_2FeMoO_{6-y} thin films of types A and B.

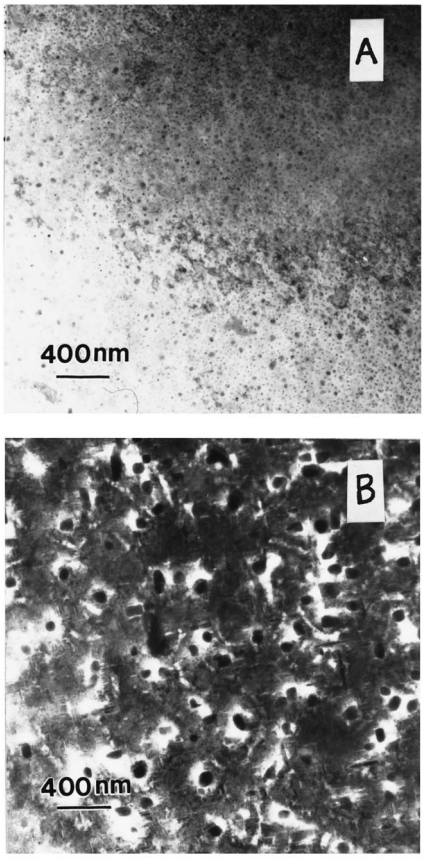

FIG. 4. Transmission electron micrographs of the Sr_2FeMoO_{6-y} films of types A and B.

analysis brought out that the clusters are highly strontium deficient with an added degree of deficiency of molybdenum. The volatility of the corresponding oxide forms appears to be the reason for this deficiency, thereby providing the chemical driving force for clustering of nonstoichiometric phases. The stoichiometry in the regions between the clusters was fairly close to the desired value (which is the target stoichiometry) within the limits of TEM based chemical analysis.

The MR of polycrystalline samples[17] is characterized by a significant low-field MR response due to the grain boundary tunneling together with a small high-field MR response. In our epitaxial films, the low-field (below 0.5 T) MR is absent because the films are free from bulk grain boundaries. The observed positive MR is quite unusual for ferromagnetic oxides. It should be noted that the behavior and situation of positive MR in Sr_2FeMoO_{6-y} resembles in several respects with that of other systems[13–15] wherein a large positive MR is reported. The important aspects include a low resistivity, a layered structure [along (111) direction], and the presence of antiferromagnetic interactions in the system. If instead of a perfectly ordered phase, a degree disordering occurs on the B sublattice, it would lead to small clusters of $SrFeO_3$ and $SrMoO_3$ distributed within the film; a granular-like configuration. The inclusion of small clusters of $SrFeO_3$ and $SrMoO_3$ could have profound implications for the magnetism and transport in Sr_2FeMoO_{6-y} because the properties and cation interactions in the parent perovskites are very different.[20,21] The compound $SrFeO_3$ has a resistivity of 1 $m\Omega$ cm and is antiferromagnetic below 130 K. On the other hand, the compound $SrMoO_3$ has a much lower resistivity of 10 $\mu\Omega$ cm and exhibits Pauli paramagnetism. Interfaces between the $SrFeO_3$ and $SrMoO_3$ regions would then provide the scenario for a possible positive MR effect. Such clustering would also explain the reduced magnetic moment observed in the case of our thin films. Moreover, the observed magnetically hard character of the effect could be explained on the basis of the role of the magnetic anisotropy associated with Mo^{5+} ion $[(4d)^1]$. Another significant feature revealed by the TEM data is the temperature dependence of the incorporation process of cations (e.g., Sr, Mo) in the film matrix. Even though the regions between the clusters show a gross stoichiometry closer to the desired value, smaller deficiencies of Sr and Mo could escape the chemical evaluation, and yet affect the transport and magnetism by influencing the mean valence.

In conclusion, we have grown epitaxial thin films of the ordered double perovskite Sr_2FeMoO_{6-y} on $SrTiO_3(001)$ by pulsed laser deposition. We show that specific physical states of the deposited films can occur which exhibit either a large positive or a negative MR. It is seen that this double perovskite structure is capable of supporting a multitude of magnetic and transport properties depending upon the ordering and defects in the Fe and Mo sublattices, vacancies on the alkaline earth (Sr) sublattice, and the oxygen concentration.

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