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In situ characterisation of Sr_2FeMoO_6 films prepared by pulsed laser deposition

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Abstract. Thin epitaxial films of the ferromagnetic double perovskite Sr_2FeMoO_6 (SFMO) have been prepared by pulsed laser deposition on $SrTiO_3(100)$ substrates under different oxygen pressures. The surface electronic structure of the as-deposited films has been analysed by XPS without exposure to the atmosphere. The films consist mainly of the *c*-axis oriented SFMO phase over a wide range of oxygen pressure from 10^{-8} to 10^{-4} mbar. However, the analysis of the films by XPS and XRD revealed the presence of different secondary phases depending on the preparation conditions. The films prepared under ultra-high vacuum conditions show the presence of metallic Fe. The films prepared under pure oxygen gas flow at pressures above 10^{-6} mbar did not show any trace of metallic Fe, but Fe_3O_4 phase. In these films XPS analysis revealed the formation of the $SrFeO_3$ phase (SFO), or another non reported Sr-containing phase, which is not observed by XRD. At higher oxygen pressures above 10^{-4} mbar there is a clear formation of $SrMoO_4$ phase (SMO). In conclusion, a ultra-high vacuum atmosphere favours the formation of metallic Fe, whereas the increase in oxygen pressure during deposition induces the decomposition of the SFMO phase to SFO and SMO phases. The conditions for the preparation of pure SFMO phase have not been attained so far, which would lie within a very narrow oxygen pressure window. Our best films (with no any other ferromagnetic phase than SFMO) show a saturation magnetisation of about 1 μ_B/f.u. at 10 K, and T_c close to 200 K. The resistivity of the films has a metallic-like behaviour and remains almost constant in the temperature range from 10 to 350 K to about 5 to 8 10^{-4} Ω cm. It was measured a magnetoresistance of about −10% at 10 T and 10 K, which coincides with the values reported in the literature for SFMO films.

1. INTRODUCTION

In the last years there has been a substantial research activity around spin-polarised half-metallic ferromagnetic manganese oxides with perovskite structure, which exhibit colossal magnetoresistance [1]. More recently ceramic samples of another oxide Sr_2FeMoO_6 (SFMO) with ordered perovskite structure and Curie temperature of about 410-450K has shown room-temperature magnetoresistance of about 10% (at 300K, and 7T) [2], which makes this material a potential candidate for developing room-temperature magnetic sensors. Several groups have reported the preparation of high-quality SFMO epitaxial films [3-7], although their exhibited physical properties are still controversial.

2. EXPERIMENTAL

The films were prepared by pulsed laser deposition. Stoichiometric SFMO ceramic targets were ablated by using tripled-Nd:YAG laser (355 nm) at a 10 Hz repetition rate, and about 3 J/cm^2 laser fluence, during 5 min (3000 pulses). Substrates were $SrTiO_3(100)$ crystals of 5x5 mm^2. Substrate temperature was kept constant during the experiment at about 950°C. The distance from the target to the substrate was 40mm. The films were prepared under different oxygen atmospheres, from a high-vacuum of 10^{-7} mbar, to 10^{-4} mbar of pure oxygen. At these conditions the growth rate of the films was about 0.2 Å/pulse. The samples were cooled down under the same oxygen flow to room temperature. XPS analysis of the chemical composition of the surface were performed immediately after deposition, and without exposure of the sample to atmosphere. This was made in order to avoid C and H_2O contamination, and further oxidation of the surface, which could obscure the real nature of the species at the surface. XRD analysis was performed on the samples after removing them from the deposition chamber. Magnetisation measurements were

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made in a dc-SQUID up to 5T. Transport properties of the samples were characterised by four-point measurements down to 4K with/without magnetic field applied (up to 10T).

3. RESULTS AND DISCUSSION

The deposited films show a mirror-like surface. However, they show a different colour depending on the oxygen pressure during the deposition. The films obtained at lower pressures, 10^{-7} mbar, without introduction of oxygen gas in the chamber, show a yellowish golden surface colour. The films prepared at oxygen pressures from 10^{-6} to three-four times 10^{-5} mbar show a black-bluish-purple colour. However, at higher oxygen pressures of 10^{-4} mbar the films look almost transparent. Figure 1 shows a SEM image of the morphology of one of the films obtained at 10^{-5} mbar O_2. The film shows a wavy surface morphology scattered by small square precipitates, which are believed to correspond to epitaxially oriented Fe oxide particles.

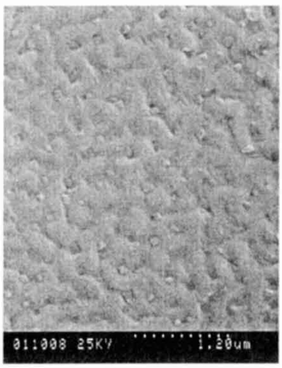

Figure 1: SEM image of the surface of a SFMO film deposited on $SrTiO_3(100)$ at 10^{-5} mbar O_2.

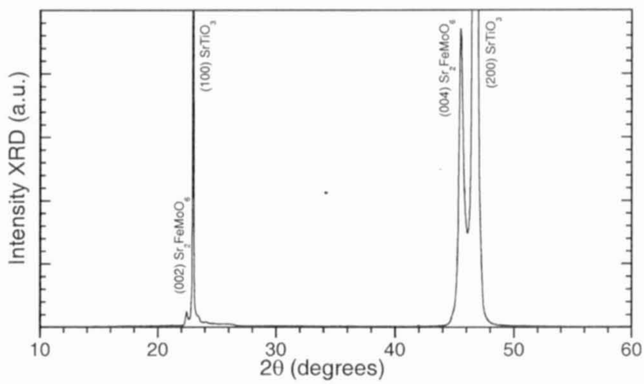

Figure 2: XRD pattern of the same SFMO film as in Figure 1. Only (00*l*) reflections are observed very close to the substrate peaks.

3.1 XRD analysis

The XRD patterns of the films show predominant (00*l*) SFMO peaks for the whole range of deposition conditions, as shown in Fig.2 for one of the films, which confirms the *c*-axis orientation of the SFMO material, with a high degree of orientation (rocking curves of the (008) peak of about 0.3 degrees FWHM) and epitaxial in-plane alignment (phi-scans of the (204) reflection show 0.6 degrees FWHM). However, a closer look to the XRD analysis evidences the presence of different secondary phases, depending on the deposition conditions, as shown in Fig.3. The sample obtained under vacuum conditions shows a weak peak at $2\theta = 65^{\circ}$ which has been identified as

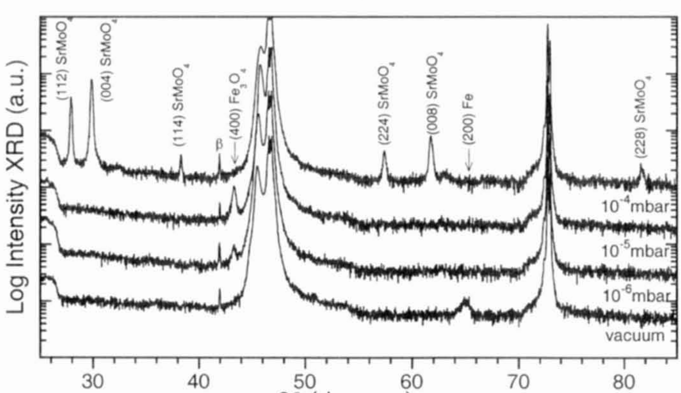

Figure 3: XRD patterns of *c*-axis oriented Sr_2FeMoO_6 films deposited on $SrTiO_3(100)$ at different oxygen pressure conditions. The labels indicate the identified reflections for the secondary phases.

(200)Fe. That peak is not present in the rest of the samples obtained under oxygen flow. Instead, for the samples obtained at 10^{-6} and 10^{-5} mbar O_2 there is another peak at $2\theta = 43.7°$ identified as (400)Fe_3O_4. At higher O_2 pressures, in the sample prepared at 10^{-4} mbar O_2, different reflections of the $SrMoO_4$ were observed. Surprisingly, no traces of Fe-containing secondary phases were observed by XRD.

Concerning the SFMO phase in the film, it did not show any clear evidence of the presence of the superstructure (101) reflection, which would indicate a poor degree of the Fe/Mo ordering.

3.2 XPS analysis

The Fig.4 shows the XPS Fe $2p$ core levels measured for the as-deposited SFMO films obtained in the same conditions as the films shown in Fig.2. The films obtained at higher oxygen pressures, 10^{-5} and 10^{-6} mbar, show a single spin-orbit doublet, with the Fe $2p_{3/2}$ peak at 710 eV binding energy, which corresponds to the reported values for oxidised Fe. This contribution may come from the Fe within the SFMO structure or any other Fe oxide. However, the film obtained under vacuum, shows an important additional contribution, at lower binding energies of 706 eV, which was unequivocally assigned to the presence of metallic Fe, in agreement with the observations by XRD.

For the same set of SFMO films we observed the variations in the Sr $3d$ core-level energies, in comparison with the same peak measured from a bare $SrTiO_3$ substrate. The substrate shows a single spin-orbit doublet with the Sr $3d_{5/2}$ peak at 132.7 eV, which is typical of most of the Sr-containing perovskite structures (Sr in A site of ABO_3) reported in the literature. The SFMO film obtained under vacuum conditions shows a similar shape, with a single spin-orbit doublet at Sr $3d_{5/2}$ of about 133 eV binding energy. However, the samples prepared with oxygen flow, at 10^{-6} and 10^{-5} mbar, show a more complex shape. They show a main contribution at about the same energies of the samples before, although the peak is slightly shifted towards higher binding energies. A weak contribution with a $3d_{5/2}$ peak at a higher energy of 134.7 eV was assigned to either SrO, or distorted structures at the grain boundaries within the film. Moreover, these samples present an additional spin-orbit doublet with the $3d_{5/2}$ peak at lower energies 131.7 eV, which increases its intensity by increasing the O_2 pressure. This observation is consistent with the formation of the $SrFeO_3$ phase (SFO) [8]. The variations in the energy of the Sr core-levels should be related to changes in the neighbouring structure of the Sr ions, rather than its valence state. From the reports in the literature only $SrFeO_3$ perovskite has shown a significant variation of the binding energies of Sr $3d$ core-levels of about 1eV. The reason that $SrFeO_3$ has not been observed by XRD is that it has a cubic structure with a cell parameter a= 3.85 Å, close matching the STO structure, and very likely to be epitaxially oriented, whose peaks would then overlap.

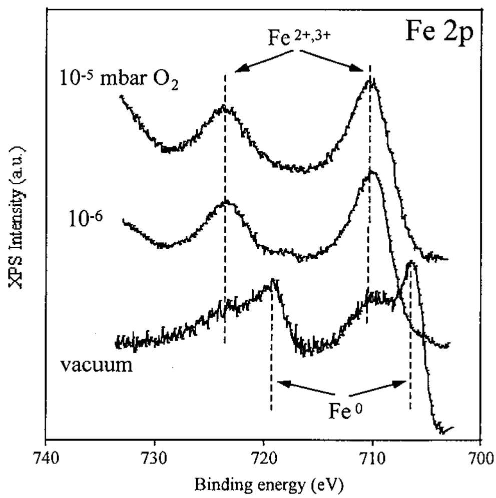

Figure 4: XPS Fe $2p$ core levels of the surface of as-deposited Sr_2FeMoO_6 films obtained at different oxygen pressures.

The formation of the SFO phase could be explained in terms of a segregation of the Fe and Mo cations, which leads to clustering of the Fe ions to form stable SFO nuclei. Since the average composition of the film is expected to remain close to the target stoichiometry, the SFO formation would lead to a local enhancement of the Mo composition, which would in turn lead to the formation of either the $SrMoO_3$ perovskite (SMO), or the more stable phase $SrMoO_4$. The latter one has been observed by XRD to form under higher oxygen pressures of 10^{-4} mbar, whereas the former one has not been even detected by XRD or XPS. The SMO phase is a cubic perovskite with cell parameter a=3.975 Å, very close to the STO and

SFMO phases, whose XRD peaks would overlap, as it happened with the SFO phase. The Sr 3*d* core-level energies for SMO and $SrMoO_4$ phases are not very different from other Sr-containing perovskite, so we would not be able to observe it in the XPS analysis. Besides, the analysis of the Mo 3*d* core levels shows a very complex combination of different contributions possibly due to the varying valence state of the Mo ion and the chemical shifts associated to the presence of different phases. This makes its interpretation very difficult and did not provide so far additional information to the identification of secondary phases.

For those reasons we can not rule out the presence of SMO perovskite even at lower oxygen pressures above 10^{-6} mbar. Although these interpretations rely on surface observations, it is very likely that the phase segregation takes place during the deposition process at high temperatures, when the mobility of the adatoms is high enough to allow surface diffusion, rather than after deposition when segregation should take place through bulk diffusion. In that case phase segregation extends to the bulk of the film, and should affect significantly the physical properties of the film.

3.3 Physical properties

The films are ferromagnetic with a T_c = 200K, significantly lower than the expected value of 410-450K for the ordered double perovskite SFMO reported for bulk material [2]. At 10K the saturation magnetisation of the films was estimated to be about 1 μ_B/f.u. as shown in Figure 5. This value is again substantially lower than the 4 μ_B/f.u. reported for the bulk material.

Figure 6 shows the variation of the resistivity of a SFMO film versus temperature. Room temperature resistivity is about 6 10^{-4} Ωcm and metallic-like. It reaches its minimum value of 5 10^{-4} Ωcm

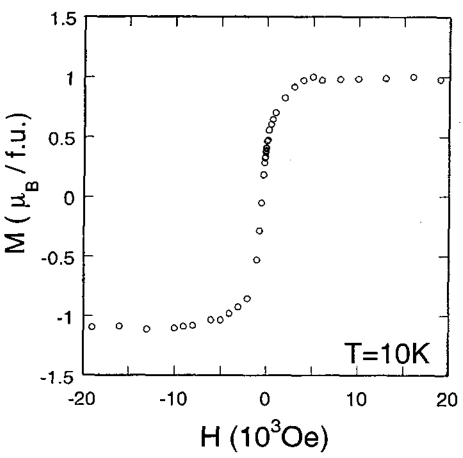

Figure 5: Magnetisation curve for a SFMO film at 10K with saturation moment of 1 μ_B/f.u., and coercitivity of 300 Oe.

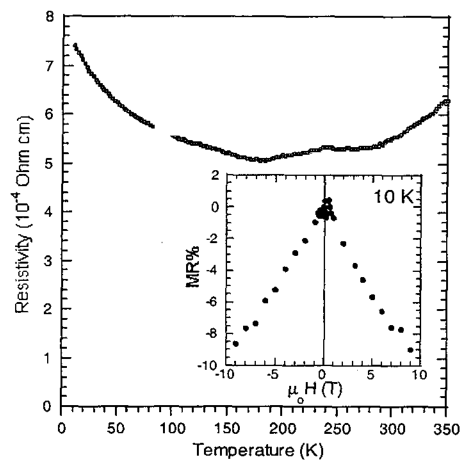

Figure 6: Resistivity versus temperature of a SFMO film. The inset shows the Magnetoresistance at 10K.

at about 200K. At lower temperatures it slightly increases up to 7 10^{-4} Ω cm at 10K. The films show negative magnetoresistance at temperatures well below T_c as shown in the inset at 10K in Figure 5; with MR of about –10% at 10T. These values are the same order of those reported in literature for thin films [4,6].

The reason for these depleted values could not be simply related to the presence of secondary phases (some of them ferromagnetic), but mainly to the residual Fe/Mo cation disorder in the SFMO structure. In SFMO bulk material, it is already known that the presence of antisite defects induces an important reduction of the magnetic moment [9,10]. In the same way, the insulating dependence of the resistivity bellow the ferromagnetic transition could be also related to the Fe/Mo cation disorder. However, the magnetoresistance at low temperatures does not seem to be particularly associated to the cationic order, as it has been recently demonstrated for bulk SFMO material, although it can be enhanced by the presence of antisite defects, and dislocations [11].

4. CONCLUSIONS

We have investigated the properties of SFMO films prepared by pulsed laser deposition under different deposition conditions, in order to elucidate which are the optimal conditions for the preparation of pure SFMO phase. The combined analysis by XPS of the as-deposited films and XRD shows the presence of secondary phases. A low oxygen pressure atmosphere during deposition induces the formation of metallic Fe particulates, whereas the increase in oxygen induces the formation of Fe_3O_4 phase, along with the segregation of SFMO phase to form $SrFeO_3$ perovskite, $SrMoO_4$ and possibly $SrMoO_3$. The presence of these secondary phases, along with the possible Fe/Mo disorder within the SFMO structure leads to reduced magnetisation of the film T_c=200K and M(10K)=1μ_B/f.u., which in turn affect dramatically the transport properties. So far we have not found the optimal conditions for the growth of pure and ordered double perovskite SFMO films, which are believed to lie in a very narrow window of deposition conditions. At this stage any characterisation of their physical properties can be obscured by the presence of some of the ferromagnetic secondary phases.

Acknowledgments

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