Magnetron sputtering of polycrystalline LSMO/YBCO structures on sapphire substrates

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Abstract. La0.7Sr0.3MnO3 (LSMO) films with different thickness were deposited directly on r-cut sapphire substrates by RF off-axis single magnetron sputtering with a view to produce a suitable buffer for growing HTS YBa2Cu3O7-δ (YBCO) films on top. These LSMO layers were polycrystalline and showed a ferromagnetic behavior at room temperatures. The top YBCO films were sputtered in a DC off-axis double magnetron system. The polycrystalline structures thus produced were characterized and discussed.

1. Introduction
Interplay between superconductivity and ferromagnetism is an interesting and exciting phenomenon because of a variety of exotic effects at the interface between these materials. Moreover, superconductor (SC) – ferromagnetic (FM) structures are of considerable practical importance. SC/FM layered structures could be used for tunable magnetic microwave devices [1–3], for dynamic modification of HTS critical parameters and for spin-polarized injection [4–7]. The oxide superconductor YBa2Cu3O7-δ (YBCO) and the doped rare-earth manganese perovskite oxides (or manganites) L1-xAxBaMnO3 (L = La, Pr,…; A = Ca, Sr, Pb,….) are promising candidates for preparing such structures.

The resistance of manganites decreases under an external magnetic field (CMR effect) due to double-exchange mechanism between 3d-electrons of Mn-ions together with a strong electron-phonon coupling (J-T polaron) [8–11]. The CMR effect gives possibility of using these materials in different microelectronic and spintronic applications [8, 9, 12–14]. The CMR effect is usually manifested at high magnetic fields (a few Tesla) in a narrow temperature range near the Curie temperature TC, which limits the possibility for conventional applications [13, 15–17]. In ferromagnetic manganites, which possess grain-boundaries (polycrystalline materials or artificial grain boundaries), a significant magnetoresistance effect is observed at low magnetic fields (tens mT) and in a broad temperature range below TC (the so-called low-field MR (LFMR) effect) [15–17]. The temperature of insulator-to-metal transition T1M in single crystals is near TC, whereas in polycrystalline material it has a much lower value [18–20].

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The aim of this work is to grow manganite La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) films on r-cut sapphire (Al$_2$O$_3$ or ALO) substrates by RF magnetron sputtering with a view to produce a suitable buffer for growing HTS YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) films on top and double layer HTS/FM structures. It should be noted that ALO is characterized by a low dielectric constant $\varepsilon \sim 10$, low electric losses $\tan\delta < 10^{-4}$, high heat conductivity and is considered as a very prospective substrate material for applications in nanoelectronics.

2. Experimental
The polycrystalline La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) thin films were deposited by RF off-axis single magnetron sputtering on double-side polished 5×10×0.5 mm r-cut sapphire (Al$_2$O$_3$ or ALO) substrates supplied by Crystal GmbH. The sputtering process was carried out in Ar:O$_2$ (1:1) atmosphere at a total pressure of 5.3 Pa. The RF magnetron power and the substrate temperature were 30 W and 780°C, respectively. LSMO films with different thickness were prepared (10, 20, 40 nm – see table 1) by varying the deposition time. After the deposition procedure was finished, an in-situ annealing at 500°C of substrate temperature and 600 Torr of oxygen pressure for 30 min took place and the sample was cooled to room temperature (RT) (at rate ~ 15 °C/min). For one of the samples (sample 5) the annealing temperature was not held at 500°C but the sample was directly cooled to RT (table 1). Thus sample 5 was less oxygenated.

As a next step, the top YBCO films were sputtered by DC off-axis double magnetron system on one half of the surface of the LSMO-covered samples. All YBCO films were of 60 nm thickness except for the case of sample 4 where the thickness of the YBCO layer was 100 nm. The standard deposition conditions were used for in-situ growth of these YBCO films.

| sample | LSMO thickness, nm | YBCO thickness, nm | CHARACTERISTICS |
|--------|-------------------|--------------------|-----------------|
| 1      | 40                | 60                 | Standard full oxidation of LSMO |
| 2      | 10                | 60                 | Standard full oxidation of LSMO |
| 3      | 20                | 60                 | Standard full oxidation of LSMO |
| 4(!)   | 40                | 100                | (!) Thicker YBCO |
| 5(!)   | 40                | 60                 | (!) Less oxidation of LSMO |
|        |                   |                    | Standard YBCO thickness |

The electrical resistance of the films was measured by a standard four-probe method from 300 K to 4 K. The presence of the ferromagnetic state in LSMO films was qualitatively confirmed by their response to the magnetic field. The magneto-optical visualization technique was used to investigate the magnetic inhomogeneities of LSMO samples.

3. Results and discussion
The LSMO films deposited on ALO substrates were polycrystalline and consisted of very small (possibly of nanometer scale) grains. These films were in the FM state at room temperature, which was confirmed by suspended samples being attracted by a permanent magnet. Moreover, an image of the edge area of the sample, obtained by the magneto-optic visualization technique (not shown here), demonstrated a brightness contrast due to the FM state of the sample. It is well known that magnetooptic (MO) visualization reveals the perpendicular component of the magnetic induction created by the magnetic defects and heterogeneity, FM domains and domain walls in the film. For example,
several types of domain structures were observed by MO visualization in our epitaxial LSMO films grown on LaAlO₃ substrates [21]. It should be noted that MO visualization did not allow us to observe clearly the domain structure in LSMO films grown on ALO substrates. In our opinion, this is due to the spatial resolution of our MO method, which is not sufficiently high to resolve magnetic patterns on a nanometer scale, as the polycrystalline LSMO films deposited on ALO consist of nanometer-scale grains and the magnetic inhomogeneities in them could be expected to be on the nanometer scale, too.

Figure 1. Electrical resistance of polycrystalline LSMO/YBCO structures: a) resistance of polycrystalline LSMO films on Al₂O₃ substrates; and b) resistance of the top polycrystalline YBCO films deposited on different LSMO underlayers. The contacts positions for the 4-point resistance measurement are shown by closed circles in the insets. The arrows show the areas measured.

Figure 2. First derivative of the resistance of polycrystalline LSMO films with a) 40 nm and b) 20 nm thickness.

The resistance versus temperature ($R$ vs $T$) dependences of these polycrystalline LSMO films are shown in figure 1a. These curves are typical for polycrystalline manganite films [18–20, 22]. In the high-temperature region, the $R$ vs $T$ dependence has a semiconductor-like behavior. At lower temperatures, an insulator-to-metal transition occurs and the resistance acquires a metallic character. Finally, an upturn of the low-temperature resistance is observed. The resistance is relatively high (in the MΩ range) which is in agreement with the results of other authors [22]. Higher values of the resistance (figure 1a) are observed for thinner films (< 40 nm). The resistance of the LSMO film with a thickness of 10 nm was too high for our measurement system and is not shown here. We assume that the grain-size of our films decreases as the film thickness is decreased in analogy with [23]. The films with a smaller grain-size possess a larger number of grain boundaries (which are a physical barrier for charge carriers) and thus demonstrate a higher resistance.
To locate the extrema of $R$ vs $T$ dependences (which correspond to the metal-insulator (M-I) peak and the upturn point of the resistance) more precisely, we calculated the first derivatives of the resistance $dR/dT$ (figure 2). The M-I peak of sample 1 (standard deposition of 40 nm LSMO) is observed at $T_{IM} = 170$ K and the upturn of the resistance, at 60 K (figure 2a). The resistance curve of sample 3 (standard deposition of 20 nm LSMO) shows a high level of “noise” and provokes a “noisy” derivative (figure 2b). $T_{IM}$ of sample 3 is approximately 170 K and the upturn minimum is observed at about 65 K. Films with the same thickness, but different degree of oxidation, possess different metal-insulator transition $T_{IM}$. It is interesting to note that the polycrystalline LSMO films with less oxidation show a higher $T_{IM}$. The resistance peak and minimum of sample 5 (40 nm LSMO, less oxidation) are 210 K and 50 K, respectively (figure 2a).

The temperature dependences of the samples resistance following deposition of top YBCO layers are shown in figure 1b. All top YBCO layers were polycrystalline and not superconducting. Actually, the resistance in figure 1b is the effective resistance ($R_{eff}$) due to the combined action of the FM and HTS layers. The resistances of FM and HTS layers ($R_{FM}$ and $R_{HTS}$, respectively) are connected in parallel: $\frac{1}{R_{FM}} + \frac{1}{R_{HTS}} = \frac{1}{R_{eff}}$. The effective resistance $R_{eff}$ of the FM/HTS structures is highly nonlinear and has an insulating character. This rise in the resistance could be due to interfacial diffusion.

When obtaining thin film heterostructures, the interfacial properties are of crucial importance. In our polycrystalline heterostructures there exist two interfaces – ALO-LSMO and LSMO-YBCO. Polycrystalline LSMO (and La$_{1-x}$Ca$_x$MnO$_3$ or LCMO) films deposited on different substrate (Al$_2$O$_3$ and Si) were investigated in [14, 18, 19, 22, 24, 25]. The magnetic and transport properties of polycrystalline LSMO (LCMO) thick films (> 100 nm) depend more strongly on the interfaces between grains than on the substrate-manganite interface. The interfaces between grains are correlated with the deposition conditions and film thickness. Recently, S. N. Kale and co-workers [26] reported on the influence of strain on the structural and surface morphology of LSMO thin films formed on Si, Al$_2$O$_3$ (ALO) and LaAlO$_3$ (LAO) substrates. The strain induced in all the systems depends essentially on the lattice misfits and on the deposition conditions as well. If the lattice misfit is high, the polycrystalline growth with a large number of grain boundaries and smaller grain size is seen to be dominating. The distortions and strain in the films on ALO are the highest and mostly due to a structural as well as dimensional mismatch. The overall growth-mode for the films on either substrate can be considered as Volmer-Weber type in which the energy relaxation takes place via the formation of 3D islands to minimize the energy. The electronic structure and magnetism of a LSMO interface buried under YBa$_2$Cu$_3$O$_7$ capping layers of various thicknesses ≤ 8 nm was investigated by Stadler et al (1999, 2000) using X-ray magnetic circular dichroism (XMCD) and X-ray absorption spectroscopy (XAS) at the Mn L2,3 edge. A comparison of the data with spectra measured on a La$_{1-x}$Sr$_x$MnO$_3$ series (Abbate et al 1992) led to the conclusion that the cation stoichiometry at the interface is changed. A YBCO overlayer facilitates a cation displacement or interchange whose net effect is the outward-diffusion of La ions: interchange of La with Ba ions or by exchange of Sr from deeper in the bulk with La at the interface. The XMCD signal is consistent with a progressive replacement of the ferromagnetic order by an antiferromagnetic structure [27, 28] which could lead to a rise in the resistance as well.

The reason why the polycrystalline YBCO layers in the polycrystalline FM/HTS structures are not superconducting could be the following. The polycrystalline bottom layer (LSMO) is very thin. Therefore, it consists of small grains and of many grain boundaries. The behavior of the resistance in polycrystalline manganites can be explained as being the result of the presence of different conduction channels. One type of channels is related to the intrinsic transport properties of the system and includes the grains with good intergrain contacts. The other type of channels includes the grains with “bad” contacts and reflects the effects of energy barriers. These inhibit metallic conduction at all temperatures due to poor connectivity and to effects of disorder and contamination in the structure [19].
The high resistance of our polycrystalline LSMO films is probably due to the presence of a great number of channels with poor connectivity between the grains, i.e., in our opinion, our LSMO layers possess poor conducting microareas: grain boundaries and physical barriers between the grains. The physical barriers appear because the grains are presumably not closely packed. The surfaces of the grains are contaminated and the Mn environment at the surface is not the same as that inside the grains [19]. Such poor conducting areas are amorphous and the superconducting YBCO crystalline phase cannot be grown on them. To minimize the poorly conducting areas and to decrease the resistance of polycrystalline LSMO films on ALO substrates, we need further optimization of the film thickness (figure 1b) and of the annealing regime. A more accurate optimization of the technology, based on structural and electrical analyses of the samples, is necessary for producing polycrystalline LSMO/YBCO thin film structures with superconducting YBCO layers.

4. Conclusion
In summary, LSMO polycrystalline films and LSMO/YBCO polycrystalline bilayer structures were obtained on r-cut Al2O3 substrates by magnetron sputtering. The LSMO polycrystalline films were ferromagnetic, but they showed large values of the resistance, especially in the case of thinner films. The top YBCO layers were not superconducting because of the presence of contaminated poorly conducting areas on the LSMO surface. These areas are amorphous and thus hinder the epitaxial growth of the superconducting YBCO phase on them.

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