Magnetic tunnels junctions for all-oxide spin valves devices

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Abstract. We have developed La₀.₇Sr₀.₃MnO₃ (LSMO) based spin valve tunnel junctions where the hard layer is composed of Ru doped La₀.₇Sr₀.₃MnO₃ (LSMRO). These perovskite oxide layers have been grown on SrTiO₃ by pulsed laser deposition. X-ray diffraction, transmission electron microscopy and atomic force microscope measurements show the crystalline quality of the La₀.₇Sr₀.₃MnO₃ and La₀.₇Sr₀.₃MnO₃ doped Ruthenium thin films. Magnetization, resistance and noise characterisation of these layers are presented. The doping of Ruthenium increases the coercitive field of the La₀.₇Sr₀.₃MnO₃ but degrades the metallic properties of the layer and leads to a noise increase of one order of magnitude. We have studied the magnetoresistance and magneto-transport properties of LSMO/STO/LSMRO–based junctions which show the importance of the interfaces quality.

Introduction

Perovskite oxides have a variety of interesting properties going from high temperature superconductivity to insulating behavior passing through magnetism, half-metallicity, ferroelectricity. Among these materials, YBaCuO (YBCO) is a cuprate exhibiting superconductivity below 92K. The manganite La₀.₇₋ₓSrₓMnO₃ with a doping level of x=0.3 (LSMO) is metallic and ferromagnetic under 340K. A high spin polarization in transport is also observed [1] and as a consequence LSMO-based tunnel junctions present a very high magnetoresistance [2], [3]. Both YBCO and LSMO present a perovskite crystalline structure and a close lattice parameter in the (a, b) plane, and are, therefore, good candidates for integrated devices. In particular, integrated epitaxial system can be designed with these oxides to develop an all oxide mixed sensor [4].

A mixed sensor is a high sensitive magnetic field sensor which uses a flux-to-field transformer to increase up to a factor of 1000 the sensitivity of a magnetoresistive sensor. The flux-to-field transformer is a superconducting ring with a small constriction which, combined to conventional metallic Giant Magneto-resistance (GMR) structure, exhibits sensitivity of few fT/√Hz in the thermal noise [5]. The gain is given by the geometry of the loop [6]. The aim is to develop a new mixed sensor which combines the performances of a high-Tc (YBCO) superconducting loop, with the high magnetoresistance of LaSrMnO₃-based tunnel junction, which would lead to a subfemtotesla magnetometer operating at 77K. A typical all oxide mixed sensor would contain

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LSMO/SrTiO₃/LSMO tunnel junction separated from the superconducting loop by a thicker SrTiO₃ (STO) insulating layer (figure 1).

\[ \text{Figure 1. All oxide mixed sensor principle: a YBCO superconducting loop with a constriction is associated to a LSMO-based TMR sensor. The field is enhanced around the ring constriction and then is measured by the TMR.} \]

A tunnel magneto resistive sensor is generally composed of two magnetic layers with different coercitive fields separated by an insulating layer in order to stabilize the antiparallel state. This structure is called a spin valve. The LSMO coercitive field can be increased by doping it with Ruthenium (Ru) (LSMRO) [7], [8] and thus a LSMRO layer can be used to create a spin valve structure [9]. In this paper, we present results on LSMO/STO/LSMRO tunnel junctions. LSMO and LSMRO films crystalline, magnetic, transport and noise properties are first described. Then, we present results on complete patterned junctions.

1. Growth

The oxide layers are grown by pulsed laser deposition (PLD) with a KrF laser (wavelength of 248nm), LSMO layers are deposited on STO vicinal substrate (100) under 120 mTorr of pure oxygen atmosphere at 600°C. In situ annealing is done at 300Torr and 600°C after the deposition. Laser energy of 200mJ allows a maximum fluence of 3J/cm² on the target. The energy is adjusted using an attenuator to obtain an average deposition flux of 0.13ML/s. An homogenizer is used to ensure a top flat profile of the laser beam on the target, and avoids formation of droplets on the surface. The thickness of the films deposited is between 25 and 44 nm. The lattice mismatch between the LSMO (\(a_{\text{bulk}} \approx 3.875\text{Å}\)) and the STO (\(a_{\text{bulk}}=3.905\text{Å}\)) is approximately 0.8%. The lattice parameter of the LSMRO depends on Ru doping [7], [10], but it is higher than the LSMO lattice parameter.

2. Single films characterizations

2.1. Crystalline quality of the thin LSMO films

\[ \text{Figure 2. a) AFM (atomic force microscope) image of LSMO layer after deposition on a vicinal STO film. b) AFM image of a LSMRO layer grown in the same conditions. c) X-Ray diffraction measurement of the same layers} \]
Figure 2 a) and b) show that the vicinal steps are transmitted from the substrate to the layers and correspond to one LSMO or LSMRO monolayer (~0.4 nm). The roughness of the layers is less than one atomic layer and is 0.1 nm RMS for the LSMO and 0.2 nm RMS for the LSMRO. The finite size effect, visible from the Kiessing oscillations around the LSMO diffraction peak (47.28°) and the LSMRO diffraction peak (46.46°) in figure 2 c), is characteristic of a good crystalline structure and of the absence of extended defects in the layers.

2.2. Magnetic and transport properties of LSMO and LSMRO

Yoke shape structures have been processed on the different layers (figure 3 c), using Ar-plasma etching neutralized under O2 and photolithography. Hundred nanometers of Pd were deposited by sputtering for metallic contacts. The resistance of the contacts is less than 1kΩ. The dimensions of the structure are 5µm x 400µm. It has been shown that the yoke structure stabilizes the magnetization along the long arm of the structure for metallic GMR [11]. Resistance measurements were performed using four probes configuration. We used a Keithley 6221 current source to bias our samples; the voltage was detected using an INA103-based DC preamplifier and an acquisition card. Magnetization versus field measurements were done with SQUID magnetometry.

![Figure 3](image)

**Figure 3.** a) Magnetic moment per unit cell (Mz) versus field at 5K. b) Resistivity versus temperature of a LSMO (square points) and a LSMRO (cross points) thin films deposited on STO substrates. c) Schematic and picture of the yoke structure which had been defined on LSMO and LSMRO layers, and allowed measuring the resistivity in four points.

We observed, in figure 3 a) an enhancement of the coercitive field by a factor of five in the LSMRO film, due to Ru doping, and also a decrease of the magnetic moment. Indeed, the Ru atoms, in the LSMRO, are in substitution on the Mn sites, and give the chemical formula La0.7Sr0.3(Mn1−yRuy)3+(Mn1−yRuy)4+O3− for low doping level (y<0.5). In our case the doping level is 0.05. LSMRO magnetic properties could be explained in terms of charge transfer and antiferromagnetic exchange coupling between Mn3+/Mn4+ and Ru3+/Ru4+ centers [7,10].

The resistivity of the LSMO varies from 1.4 mΩ.cm at 300K down to 0.14 mΩ.cm at 4 K. An increase of resistance is observed for the LSMRO film around 90K, probably due to polaron hopping, and charge career localization [10]. So doping by Ru degrades the transport properties of the layer, despite the good crystalline features given by X-Ray analysis and surface roughness.

2.3. Noise measurements

For sensor applications, noise is as important as sensitivity. Noise is also another way to probe transport properties. Johnson noise due to thermal excitations and shot noise due to current fluctuations are independent of the frequency f. Another noise source is the 1/f noise. It is due to
resistance fluctuations in small volumes and hence is proportional to the current and inversely proportional to the square root of the number of carriers. Noise measurements are done with an AC coupled low noise amplifier and a battery fed current source. From Figure 4 a), it appears that 1/f noise is dominant on the yoke structure at frequency lower than 1kHz. Johnson noise level can be measured from the noise power spectrum at zero bias current.

Figure 4. a) Voltage noise spectral density in a LSMO yoke (thickness 28nm) at 110K. Johnson noise is present with zero current. 1/f noise appears when a current is applied and increases linearly with the current square (inset). b) Voltage noise spectral density normalized by the voltage and the volume in LSMO (thickness 28nm) and LSMRO (thickness 44nm) yokes at 110K.

To compare noise from different samples, the $\alpha$ parameter from the empirical Hooge formula (equation (1)) is used.

$$\alpha = \frac{S_V(f) f^\alpha V_{DC}}{V_{DC}^2 \tau_H} = \frac{\gamma_H}{n_c}$$

The noise spectral density, $S_V(f)$, depends on the sample voltage $V_{DC}$, the sample volume $V_{o}$, the density of careers $n_c$ and the Hooge constant $\gamma_H$.

For our LSMO samples, $\alpha$ is $3 \times 10^{-37}$ m$^3$ at 150K; this noise is higher than the best results presents in the literature. For instance, A. Palanisami et al. achieved $2 \times 10^{-32}$ m$^3$ [12] and L. Mechin et al. $8 \times 10^{-31}$ m$^3$ [13] but in the average of the broad range of noise value [14] published (from $10^{-32}$ m$^3$ to $10^{-30}$ m$^3$). The noise level measured in LSMRO yoke is one order of magnitude bigger than in the LSMO yoke (figure 4 b)). The origin of the degradation of the conductivity might also explain the increase of noise in the LSMRO. Polaron hopping and charge careers localization could be responsible of this larger low frequency noise.

3. Magnetic tunnel junctions results

LSMRO/STO/LSMO junctions on STO substrate, with thicknesses of 30nm/4nm/30nm, have been produced by PLD with the same conditions than before. These junctions were processed with UV lithography to design square junctions of $8\mu m \times 8\mu m$. The shape of the overall structure is shown in figure 5 a). The junctions’ resistance were measured in four points. The typical RA product (where $R$ is the tunnel resistance and $A$ is the area of the junctions) measured are in the G$\Omega$.µm$^2$ range. For practical application, this product should be reduced, by decreasing the thickness of the STO barrier. We estimate the barrier height to 0.1 eV by fitting the IV curves measured at 300K with the Brinkmann model [15]. This value is smaller than the barrier height reported in the literature, around 0.5eV [16], and could indicate the presence of impurities in our barrier, probably oxygen vacancies. TMR versus field, voltage bias and temperature, is shown in figure 5.
could explain the decrease of \( H_c \) by the interface between STO and the LSMRO layer is the hard layer but the coercitive field is smaller than the processed full layer, but also after patterning in a 8x8µm² junction. Nevertheless, the LSMO doped by Ru totally stabilizes the anti-parallel state.

A peak of the TMR is observed at zero bias up to 160%, as well as a sharp decrease of the TMR with the voltage bias. At 100mV, no more TMR is observed. This behavior is usually explained by the interaction of electron with magnons in the tunneling process [17], i.e. inelastic tunneling, but also by the presence of metallic particles, magnetic impurities or multi-step tunneling stage in the barrier or at the interface [18]. In our opinion, the presence of Ru at the interface between STO and the LSMRO could be at the origin of the quick decrease of the TMR with voltage observed in these junctions. We observed an increase of the resistance versus temperature for most of the junctions measured (Figure 5 d) insert) which is a typical behavior for junctions [19].

The TMR decreases when the temperature is raised and disappears above 140K. J. S. Moodera [18] proposed that the two principal mechanisms that could explain the temperature dependence of the TMR: spin-flip scattering of tunneling electrons from impurities in the barrier or a reduction of the

Figure 5: a) Schematic of the junction realized by UV photolithography. The junction is a square of 8µmx8µm. b) TMR at 5K and the magnetization versus field of the same sample before processing at 5K. The LSMRO layer is the hard layer but the coercitive field is reduced by the process. a) TMR as function of the voltage bias applied. b) TMR and RA product in the parallel and the antiparallel state (inset) of the junction versus temperature. A 50 mV constant voltage bias is applied, and the current is measured.

4. Discussion

LSMO/STO/LSMRO junction has a spin valve structure behavior before processing in the full layer, but also after patterning in a 8x8µm² junction. We observe a decrease of the coercitive field \( H_c \) due to the processing. Ishii et al. [9] observed in LSMO/LAO/LSMRO junctions an \( H_c \) of the full layer smaller than the processed junctions, and they did not find correlation between \( H_c \) and the geometric shape anisotropy. We could explain the decrease of \( H_c \) by a non homogeneity of Ru doping or a migration of the Ru during the junction processing. Nevertheless, the LSMO doped by Ru totally stabilizes the anti-parallel state.
magnetic moment in the ferromagnet due to excitation of magnons. Nevertheless, in LSMO, it is known that a loss of the magnetization appears at the interfaces [20]. This could explain the TMR temperature variation in a more relevant way.

Conclusion

We have grown LSMO and LSMO doped Ru thin films and we have studied their crystalline, magnetic and transport properties. The Ru doping hardens the LSMO layer but degrades the transport and noise properties in the studied films. We have processed and measured tunnel junctions based on LSMO/STO/LSMRO. Firstly the LSMRO layer allows creating a spin valve structure. But it seems that the Ru plays an important role at the interface of the junction and may be at the origin the TMR peak at zero bias and the rapidly decrease of the TMR with voltage bias and temperature. To avoid these effects a simple solution could be to add a LSMO spacer (~2nm) between the STO and the LSMRO. This spacer could avoid the effect of the Ru present at the interface while keeping the enhancement of the coercitive field.

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