Co-doped (La,Sr)TiO$_{3-\delta}$ : a high-Curie temperature diluted magnetic system with large spin-polarization

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The research of ferromagnetic semiconductors is an important challenge in nowadays spintronics. Since ferromagnetic properties have been found in Mn-GaAs [1], several types of other diluted magnetic semiconductors have been investigated. The discovery of room temperature ferromagnetism in Co-doped anatase TiO$_2$ [2] has triggered an intense research on other diluted magnetic oxide systems (DMOS). Some recent experiments have also suggested the existence of ferromagnetism in La$_{1-x}$Sr$_x$TiO$_{3-\delta}$ doped with Co [3, 4] i.e. a DMOS in which the host oxide is not a semiconductor but a strongly correlated metal [5]. Several models of ferromagnetism have been proposed for these DMOS, including models based on a new type of exchange interactions via shallow donors (associated with oxygen vacancies) [6]. Application of DMOS to spintronics requires not only ferromagnetism but also spin polarization of the carriers. This spin polarization can be studied by several techniques. For instance, X-ray magnetic circular dichroism is one of the best tools to detect the coupling between delocalized sp-carriers and localized d-electrons and was successfully applied in transition metal doped ZnO [7]. On the other hand, it has been argued that anomalous Hall effect (AHE) should be observed in these compounds. Nevertheless, the concomitant observation in Co-doped TiO$_2$ of parasitic superparamagnetic metallic Co clusters and AHE has cast doubts on the usefulness of AHE to unambiguously demonstrate intrinsic spin-polarization in DMOS [8]. A more direct way is provided by tunneling magnetoresistance (TMR) measurements that can probe directly the spin polarization involved in spintronics experiments. This is the way we have taken to investigate the ferromagnetism and the spin polarization in the (La,Sr)Ti$_{1-\delta}$Co$_x$O$_{3-\delta}$ (Co-LSTO, x=0.01) DMOS.

In this Letter we thus report on the growth of Co-LSTO films, their magnetic and structural characterizations, on the fabrication of tunnel junctions composed of Co-LSTO and Co electrodes separated by a LaAlO$_3$ (LAO) barrier and on the TMR experiments performed on these junctions and their interpretation.

We have deposited Co-LSTO epitaxial thin films on SrTiO$_3$ (001) substrates by pulsed laser deposition (PLD) [9] from a target with composition La$_{0.37}$Sr$_{0.63}$Ti$_{0.98}$Co$_{0.02}$O$_3$ (i.e. x=0.02). The heterostructures elaborated for the definition of MTJs were fabricated by first growing Co-LSTO(150 nm)/LAO(1.6 nm) bilayers at P$_{O_2}$ = 6×10$^{-7}$ mbar by PLD and subsequently sputter-depositing ex-situ a Co(12 nm)/CoO(3 nm)/Au(15 nm) stack. The CoO was intended to magnetically pin the top Co-electrode by exchange bias. The heterostructures were then patterned into MTJs with size ranging from 6 to 128 $\mu$m$^2$ by an advanced photolithography process [10].

We have investigated the structural properties and the homogeneity of the chemical composition of various Co-LSTO films by combining several advanced characterization tools. Auger electron spectroscopy (AES) mappings were performed over regions of size up to 10×10 $\mu$m$^2$ to detect La, Sr, Ti, O and Co elements. The resulting elemental mappings were homogeneous and did not show any contrast (see for instance a mapping for Co in the
FIG. 1: Auger intensity for several elements, measured as a function of the sample etching time, for a Co-LSTO film of thickness $t = 130$ nm grown at $P_{O_2} = 6 \times 10^{-7}$ mbar. Inset: AES mapping of Co in the same film.

inset of Fig. 1. The AES signals were also measured in real-time while sputtering the films with Ar ions accelerated at 2 keV, see figure 1. The AES signals remain roughly constant, indicating a homogeneous distribution of the different elements, until a sputtering time of about 50 min when the La and Co levels decay steadily to zero, while the Sr and Ti levels increase and then stay constant. This signals the interface between the Co-LSTO film and the STO substrate. The level of the Co was estimated to be around $x = 0.01$, which is somehow lower than the nominal $x = 0.02$.

We have also investigated the microstructure of Co-LSTO thin films using transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) experiments combined with electron energy loss spectroscopy (EELS) measurements. No parasitic phase (e.g., Co clusters) was detected by TEM or HRTEM. In Fig. 2a, we show a HRTEM image of the Co-LSTO/STO interface in the [100] zone evidencing a good epitaxial quality. The absence of Co clusters was further confirmed by low-magnification EELS elemental mappings in cross section (see in Fig. 2b-d). The signal in the Co image is pure noise in the used recording conditions (0.5 s pixel$^{-1}$).

Finally, we have also analyzed the fine structure of the Ti-edge in the EELS spectra, which is characteristic of its valence. We estimate the 3$^+/4^+$ ratio in our samples by considering the Ti-edges we have recorded (Fig. 2e), as a linear combination of the edges of pure T$^{3^+}$ and T$^{4^+}$ recorded on standards with approximately the same energy resolution (0.8 eV). We find a 3$^+/4^+$ ratio of $\sim 3.1$, corresponding to an average valence of $\sim 3.25^+$ for the Ti ions. If we assume the La/Sr ratio to be $\sim 0.58$ as in the target, the Ti valence should be $\sim 3.63^+$. This difference can be explained by the presence of oxygen vacancies promoted by the low growth pressure, creating electrons that populate the Ti 3d band. The oxygen deficiency necessary to account for a valence of 3.25$^+$ is $\delta \approx 0.19$ that is close to the value found by Muller et al., in SrTiO$_3$-$\delta$ films grown in similar conditions.

To summarize this structural part, we can conclude from the HRTEM pictures and the elemental mappings obtained by AES and EELS that the films are of very good structural quality, with no extended defects and, more importantly, that the Co distribution is homogeneous in the film. No Co-rich regions larger than $\sim 10$ nm are present.

In Fig. 3a, we show a typical ferromagnetic hysteresis cycle measured at room temperature for a 130 nm Co-LSTO film grown at $P_{O_2} = 6 \times 10^{-7}$ mbar. The saturation magnetization ($M_S$) for this film is about 4.5 emu.cm$^{-3}$ and was found to increase when $P_{O_2}$ decreased from $P_{O_2} = 5 \times 10^{-4}$ to $6 \times 10^{-7}$ mbar. This suggests some role of oxygen vacancies on magnetism. From the Co
the magnetization of the low-P 4K and bias-voltage of 50 mV. That the magnetization of the Co-LSTO layer is almost clearly observed in the antiparallel state, which suggests the mesa structure of the junction. Note that a plateau is electrode, to the dipolar field generated by the Co layer in the CoO layer on the Co electrode and, for the Co-LSTO H = 0 axis, which is due to the exchange bias induced by the presence of ferromagnetic Ti, as indicated by observation of some preliminary nuclear magnetic resonance (NMR) measurements on our Co-LSTO films showing the presence of ferromagnetic Ti, as indicated by observation of 47Ti and 49Ti NMR signals corresponding to a hyperfine field of 12T at 4.2 K [13].

Figure 3 shows a TMR curve recorded at 4 K in one of our Co-LSTO/LAO/Co/CoO/Au MTJs (size: 64 μm²). The curve was obtained at Vbias = 50 mV after field cooling in 6 kOe. The R(H) curves are shifted respect to the H = 0 axis, which is due to the exchange bias induced by the CoO layer on the Co electrode and, for the Co-LSTO electrode, to the dipolar field generated by the Co layer in the mesa structure of the junction. Note that a plateau is clearly observed in the antiparallel state, which suggests that the magnetization of the Co-LSTO layer is almost saturated in this field range under the action of the applied field and the dipolar field induced by the Co layer. The I(V) curves (see Fig. 3b) are non-linear, indicative of tunnel transport. Our first conclusion is that large TMR effects (up to ~19%) are observed and demonstrate the spin polarization of the carriers in the Co-LSTO electrode. The existence of such spin-polarization as well as a robust magnetism for a Co concentration of ~1 at% allows excluding short-range interactions such as conventional super-exchange or double-exchange to be at the origin of ferromagnetism in this compound. We discuss below the quantitative determination of the spin polarization.

A striking result of our tunneling experiments is the bias dependence of the TMR, see figure 4. This type of bias dependence is usually observed when there is a significant contribution of impurity-assisted (or defect-assisted) tunneling. A clear interpretation of this bias dependence has been given by Tsybulev et al. for Ni/NiO/Co nanojunctions in which the small size (0.01 μm²) of the junctions allowed these authors to assume resonant tunneling via a single localized level (a single level in a given junction) [14]. Here we use the extension of the model worked out by Garcia et al. [15] to describe the situation with still single-impurity-assisted tunneling but localized levels distributed in a band. In our junctions, the localized levels could be due to O vacancies but localized levels distributed in a band. In our junctions, the localized levels could be due to O vacancies but localized levels distributed in a band. In our junctions, the localized levels could be due to O vacancies but localized levels distributed in a band. In our junctions, the localized levels could be due to O vacancies but localized levels distributed in a band.
G(σ, σ′) = \frac{4e^2}{h} \frac{Γ_{LO}/h + Γ_{Rσ′}}{Γ_{LO}/h + Γ_{Rσ′} (\varepsilon - \varepsilon_C)^2 + (Γ_{LO}/h + Γ_{Rσ′} + W)^2}

where \(Γ_{LO}/h, Γ_{Rσ′}/h\) are the leak rates of an electron from the localized state into the left (L) or right (R) electrode, respectively, and \(σ, σ′\) refer to the spin state (↑, ↓) of the left (right) electrode. This resonant tunneling model includes six parameters, namely, \(Γ_{LO}, Γ_{Rσ′}, W, ε_C\). The spin polarizations of the leak rates, \(P_L = (Γ_{L↑} - Γ_{L↓})/(Γ_{L↑} + Γ_{L↓})\) and \(P_R = (Γ_{R↑} - Γ_{R↓})/(Γ_{R↑} + Γ_{R↓})\) are the spin polarizations of the left and right electrodes. All the TMR dependencies can be fitted with Eq. (1) and with a convenient set of parameters, which indicates that the main contribution to the tunneling comes from this process. We show a typical example in Fig. 4a.

The most remarkable result is that we extract almost the same spin-polarization for each electrode from fits of the bias dependence of TMR in several junctions, i.e. \(P_L = -0.25±0.05\) and \(P_R = -0.8±0.02\), which we cannot determine the sign of each polarization. However, preliminary TMR measurements obtained on La\(_{2/3}\)Sr\(_{1/3}\)MnO\(_3\)/LAO/Co MTJs indicate a negative spin polarization of about \(P \approx -15\%\) at the Co/LAO interface. We can thus consider that both \(P_L\) and \(P_R\) are negative and that the smallest spin-polarization (in absolute value) corresponds to that of the Co/LAO interface, that is \(P_{Co/LAO} = -0.25±0.05\). This therefore implies a spin-polarization of \(-0.8±0.02\) for the Co-LSTO/LAO interface. This remarkably high spin polarization found at the Co-LSTO/LAO interface undoubtedly argues for an intrinsic origin of ferromagnetism in Co-LSTO.

The last question is the origin of these impurity states. We recall that in order to optimize the magnetic properties of the Co-LSTO films the Co-LSTO/LAO bilayers were grown at extremely low oxygen pressures \((6×10^{-7}\) mbar). Thus, the barriers were not grown in standard conditions, and very likely contain oxygen vacancies that create defect states within the LAO gap. In Fig. 4b, we present the temperature dependence of the TMR of a 12 μm\(^2\) junction at \(V_{bias} = 20\) mV. The TMR decreases rapidly with T and becomes vanishingly small above 200 K. This behavior is unexpected since Co-LSTO is ferromagnetic at 300 K (see Fig. 4b) and the Curie temperature of Co is far above room temperature. There are several possible origins for this behavior. First, we note that the pinning by exchange bias of the Co-top electrode in our structures disappears at T > 150 K, which can lead to very similar values of the coercive fields of Co and Co-LSTO above this temperature and, consequently, to the absence of a field range with antiparallel orientation. Another origin may be related to the onset of thermally assisted spin flips on impurity levels inside the barrier, which may be detrimental to the spin polarization of the tunneling current as observed in MnAs/AlAs/MnAs MTJs. In a model of resonant tunneling through localized states as well as in the case of sequential processes through an energy band, TMR subsists unless the tunneling time \(τ_n = h/(Γ_L + Γ_R)\) of the particle exceeds its spin lifetime \(τ_{sf}\). The rapid decrease of TMR with temperature might indicate the effects of some thermally-assisted spin flip mechanisms drastically shortening the spin lifetime with temperature. Finally one must not discard the possibility of a degradation of the spin polarization at the Co-LSTO/LAO interfaces, as observed in other ferromagnetic oxides. More experiments are foreseen in order to clarify the role of the Co-top electrode pinning or the impurity levels in the barrier in both the bias and temperature dependence of the bias and temperature dependence of the Co-LSTO-based MTJs.

In summary, we have reported on TMR results indicating a significant spin polarization of the diluted magnetic oxide system Co-LSTO. By HRTEM, EELS, AES and AGFM measurements, we exclude Co-segregation as the origin of the ferromagnetism and TMR in Co-LSTO, and we conclude that the spin-polarization as well as the ferromagnetism are intrinsic properties of this DMOS. Our results bring strong arguments for the DMOS approach with complex oxide materials in spintronics.

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