LSMO - growing opportunities by PLD and applications in spintronics

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Abstract. Ferromagnetic materials exhibiting at room temperature combination of good conductivity, magnetic and opto-electronic properties are needed for the development of functional spin-devices. Mixed-valence LSMO is an optimal source of fully spin-polarized carriers and shows a rich physics of magnetic phases and transport mechanisms. Many factors, such as growth temperature, oxygen stoichiometry, temperature-dependent oxygen desorption rate, structural matching between the growing film and substrate, film thickness, and defects, influence the LSMO properties. Stabilization of ferromagnetic and conductive behaviours is linked to structural order. Therefore a growth approach allowing congruent deposition of complex materials under controlled, reproducible and tunable conditions is strongly needed. In this respect pulsed laser deposition reveals a well-suited choice. This review aims to give an overview on LSMO thin film properties, deposition and applications, especially in the emerging organic spintronics.

1. Introduction
Spintronics has recently attracted large interest since the use and effective manipulation of the electron spin as a further degree of freedom brings significant advantages and new device functionalities as compared to conventional electronics. Improvements include increased effectiveness in performing mass storage, logic operations and quantum computing as well as non-volatility, low power operation and high switching speeds [1-4]. Recently, research also focused on spin-LED and spin-OLED devices, due for example to the possibility of overcoming the recombination statistic constraints in organic semiconductors through injection of spin-polarized carriers [5-9]. In particular for spin injection and detection in spin-valves as well as efficient spin-OLEDs, it is essential to match crucial requirements such as electrodes exhibiting room temperature ferromagnetism, good opto-electronic properties and work-function alignment with states in the organic layer. In this scenario, optimal magnetic materials for high performance spintronic devices are half-metals as sources of fully spin-polarized carriers [10-13]. In particular, Stoner splitting of spin-up and spin-down subbands can provide half-metallic behaviour to transition metal oxides because of their narrow conduction bands (~1eV) and well known examples are CrO\textsubscript{2}, La\textsubscript{0.7}Sr\textsubscript{0.3}MnO\textsubscript{3} (briefly termed LSMO), the double perovskite Sr\textsubscript{2}FeMoO\textsubscript{6} and the ferrimagnet Fe\textsubscript{3}O\textsubscript{4} [14]. Among them mixed-valence manganese perovskites were intensively studied since their discovery in the fifties because of their rich physics and unconventional magneto-transport properties, such as ferromagnetism associated to metallic conduction and the occurrence of large negative magnetoresistance [14-17]. For this reason, they

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attracted a lot of interest for both fundamental studies and technological applications [3, 17-19]. In this context, LSMO is a particularly attractive half-metal manganite and pulsed laser deposition (PLD) [20-23] is a very versatile deposition technique to master film properties. Here, the fundamental and practical issues of the peculiar coupling among charge, lattice and spin which characterizes LSMO are discussed with respect to the interplay among material critical parameters and microstructure. Moreover, selected examples of spintronic devices involving LSMO are reviewed with particular attention to the emerging field of organic spintronics [24], but without the aim to be exhaustive since the field is rapidly growing. In general, the flexible tuning of the LSMO film microstructural features allowed by PLD is crucial in favouring stabilization of the ferromagnetic as well as conductive behaviour.

2. LSMO transport and magnetic properties
Half metallic ferromagnets are ideal materials for spintronics due to their ability to provide nearly 100% spin-polarization which results in effective spin-injection, high magnetoresistance (MR) and an enhancement of all spintronics effects in general [10-13]. As an instance, single spin channel injection is a key chance in developing spin-dependent tunnelling devices [25-28] and to improve the electroluminescence efficiency of OLEDs by tuning recombination statistics [29-32].

Among manganese perovskite oxides La$_{1-x}$A$_x$MnO$_3$ (where A = Ca, Sr, Ba) has been widely investigated as an optimal material for spintronic devices thanks to its low carrier density ($10^{21}$ - $10^{22}$ cm$^{-3}$), high carrier spin-polarization, highest Curie temperature ($T_c = 370$K in the bulk) among mixed-valence manganites and colossal magnetoresistivity (CMR) [11, 12, 25, 27, 33, 34]. Figure 1 shows the basic LSMO perovskite crystal structure that, in first approximation, can be viewed as a face centered cubic lattice with a Mn-site at the centre surrounded by six oxygen site anions forming an octahedric structure (oxygen octahedron), and La/Sr cations at the corners of a cube. As matter of fact, the stable unit cell is a distorted face centered cubic lattice structure, due to the occurrence of distorted oxygen octahedron. LSMO structural stability is determined by the charge neutrality criterion and tolerance factor that also depends on the Sr dopant radius. In the LSMO lattice, the rare earth trivalent ions are the larger sized species, while the smaller Mn ions occur in the mixed-valence Mn$^{3+}$-Mn$^{4+}$.

In the ideal perovskite structure, the crystal field splits the five $d$ orbitals of an isolated Mn ion into a $t_{2g}$ triplet (consisting of the $d_{xy}$, $d_{xz}$ and $d_{yz}$ orbitals) and an $e_g$ doublet (originating from the $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ orbitals) whose degeneracy is further lifted by lattice distortions lowering the crystal symmetry (namely Jahn-Teller distortions, as discussed later). Due to the tetrahedral Mn-O coordination the $t_{2g}$ triplet is energetically lower than the $e_g$ doublet as shown in figure 2(a). The spin resolved band

Figure 1: Basic crystal structure of the LSMO perovskite manganite. The oxygen octahedron around the Mn ions in the mixed valence Mn$^{3+}$ to Mn$^{4+}$ is also shown.
The structure corresponding to this simple level model is sketched [12, 35] in figure 2(b), where the Jahn-Teller distortion-induced lifting of the two-fold degeneracy of the $e_g$ spin-up and spin-down bands is also shown. Hence, in the Mn$^{4+}$ valence states the low-lying $t_{2g}$ states are occupied by three parallel-spin electrons forming a $S = 3/2$ core spin while in the Mn$^{3+}$ valence state ($S = 2$) the additional electron occupies the higher-lying $e_g$ states (with crystal field splitting $\Delta \approx 1.5$ eV between the lowest $t_{2g}$ and the highest $e_g$ level). Basically, substitution of divalent Sr$^{2+}$ for La$^{3+}$ in LaMnO$_3$ causes an equal number of Mn$^{3+}$ to convert to Mn$^{4+}$ and proportionally induces itinerant holes with carrier delocalization in the ferromagnetic phase for a doping concentration of nearly $x = 0.3$. Doped manganites with $x < 0.5$ ($x > 0.5$) have a conduction band more (less) than half filled and are referred to as hole-doped (electron-doped). In hole-doped LSMO the spin-up localized $t_{2g}$ band is fully occupied, whereas the spin-up $e_g$ band is partially occupied and they are completely separated from the empty minority bands by a large Hund’s energy ($\Delta \approx 2.5$ eV). The oxygen $2p$ states are fully occupied for both spin states and the electronic structure near the Fermi level is determined by the hybridization between the bands associated to the majority spin Mn $e_g$ states and the oxygen $p$ states. As an insulating band gap separates the minority-spin-states and the oxygen $2p$ band, the LSMO spin-polarized density of states has only majority carriers at the Fermi level. Hence LSMO is a half metal.

As a function of temperature, mixed-valence LSMO shows a metal-insulator (MI) transition as other doped manganites [12, 36, 37]. The metal-insulator transition temperature $T_{MI}$ (that is the peak in resistivity curve versus temperature) and the Curie temperature $T_c$ are both connected to electronic distribution of spin-up and spin-down states and width of the impurity band. Transport regimes and magnetic properties are critically influenced by dopant size and content determining the tolerance factor and average Mn valence, by the relative alignment of the carrier spin to the localized Mn ions and by the structural order related to the growth method and conditions. The two critical temperatures $T_{MI}$ and $T_c$ can coincide, although this is not a universal property of all of the manganites [38].

A qualitative explanation for the metallic conduction below $T_c$ and insulating behaviour above $T_c$ is provided by the "double exchange" (DE) mechanism [39-41] consisting of the ferromagnetic (FM) interaction (through conduction electrons) between the localized 3d magnetic moments with strong on-site Hund’s coupling. Accordingly, the relative alignment of adjacent localized spins on the manganese atoms rules the dynamics of itinerant carriers. Charge transport is mediated by the hopping

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**Figure 2:** (a) Crystal field splitting of the Mn ion $d$-levels in the perovskite crystal and electronic occupation of the mixed valence Mn ions. The degeneracy of the $e_g$ and $t_{2g}$ levels is lifted by both axial elongation and planar compression as well as axial compression and planar expansion of the oxygen octahedron around each trivalent Mn ion. (b) Sketch of the spin resolved band diagram with lifted degeneracy of the $e_g$ bands.
of electrons between adjacent Mn$^{3+}$ and Mn$^{4+}$ eg states along the Mn$^{3+}$-O$_2$-Mn$^{4+}$ chains. However, the hopping probability is largest when the manganese spins are parallel (figure 3(a)) to each other and smaller otherwise (figure 3(b)). As a result, carriers move easily through the ferromagnetically ordered Mn core spins in the ferromagnetic phase, while in the paramagnetic phase above T$_c$ they are localized due to randomly aligned Mn spins. Consequently, any mechanism capable of suppressing/increasing the spin disorder, such as a magnetic external field or thermal fluctuations, would increase/decrease carrier mobility and lead to a change in the electrical resistivity (e.g. a MR effect). However, this simple spin-dependent electron hopping mechanism fails to explain other experimental observations like the high-temperature insulator-phase [42-44] or the slight difference between the critical temperatures T$_{MI}$ and T$_c$.

The DE and the localization of itinerant carriers by Jahn-Teller (JT) distortions [45] of the oxygen octahedron surrounding each manganese atom can explain conductivity below T$_c$ and high resistivity around the T$_{MI}$ as well as the observed CMR. Within this model, elongation or compression of the oxygen octahedron occurs due to the spontaneous tendency of trivalent Mn$^{3+}$ to distort its octahedral environment to lift orbital degeneracy. Indeed, the Mn$^{3+}$ degenerate electronic bands $e_g$ make the ideal oxygen octahedron geometrically unstable and cause structural distortions lowering the crystal symmetry. The consequence is a splitting of the $e_g$ and $t_{2g}$ degenerate orbital levels as shown in figure 2(a). In particular, JT distortions lift the two-fold degeneracy of the $e_g$ bands, leading to a doublet of $e_g$ bands which are energetically separated for each spin-channel (figure 2(b)). While the energy of Mn$^{4+}$ remains unchanged, the reduced energy of Mn$^{3+}$ localizes electrons in the paramagnetic phase leading to an insulating behaviour, whereas the increased carrier band width in the ferromagnetic state quenches the JT localization effect inducing metallic conduction.

The JT effect leads to (JT) lattice polarons through a charge-lattice interaction which traps electrons. The concept of polaron is more general since different mechanisms can lead to carrier trapping while the strength of the charge-lattice coupling determines the polaron nature. To explain charge transport and the mid-infrared excitation in the optical conductivity, large polarons (LP) and small polarons (SP) must be invoked [35, 46-48]. Specifically, LP transport is ruled by a self-trapped carrier excited from a trapped ground state to the continuum of unbound states. Conversely, if electron-lattice coupling is sufficiently strong, a SP is excited from its well localized ground state to another well-localized state located on an adjacent site. In both cases, a characteristic energy is needed to either free the self-trapped LP or induce the inter-site SP transition [46, 47]. For high temperatures, the dc-conductivity law for SP hopping is thermally activated over the potential barrier between adjacent sites. In disordered materials, where the carriers are localized by random potential

![Figure 3:](image)

**Figure 3:** According to the DE model, the electronic transfer probability is (a) maximum when the spin of the Mn$^{3+}$ and Mn$^{4+}$ ions are parallel and (b) increasingly suppressed as the spin misalignment of the Mn$^{3+}$ and Mn$^{4+}$ ions increases.
fluctuations, the SP hopping can occur between the nearest sites with large energy differences or between sites beyond the nearest neighbours with small energy difference. In this respect, in polycrystalline manganites the preferentially conductivity regime is the variable range hopping (VHR) corresponding to SP hopping between farther sites with a smaller potential difference and lying within a certain range of energies [48]. As a result, above T_c, an Arrhenius law describes the temperature dependence of the resistivity which exhibits thus a thermally-activated behavior [49-51].

Concerning MR, for single crystals and epitaxial layers MR values approaching to zero at the lowest temperatures and CMR only under application of strong magnetic fields were reported [11, 52, 53]. On the contrary, large low-field MR (LFMR) effects have been reported in polycrystalline bulk and thin films at low temperature [54-58]. These different behaviours observed in the ferromagnetic regime, depending on the microstructure of the material, cannot be explained by the DE mechanism too. The enhanced LFMR response in polycrystalline samples can be ascribed to spin-polarized tunnelling (SPT) between grains [25, 34, 55-57] or spin-dependent scattering (SDS) across interfaces or grain boundaries (GBs) [58-60].

Basically, whereas below T_c the conduction electrons (almost completely polarized inside a magnetic domain) are easily transferred through the Mn–O–Mn chains, spin-disorder dependent scattering at the GBs induces a high zero-field resistivity. Indeed, the magnetization configurations in the polycrystalline materials are differently distributed depending on the grain-magnetic domain structures and magnetically disordered regions occur near the GBs. Such distribution of canted spins acts as insulating and spin-scattering zone. Therefore, electrons can hop from a magnetic domain to another through an intermediate thin insulating layer by spin-dependent tunnelling with a probability essentially depending on the spin states in the neighbouring grains on each barrier side as well as the spin order of the inter-grain zones. This process is similar to transport in a magnetic tunnel junction (spin-valve) as sketched in figure 4, with parallel and antiparallel magnetizations resulting in low resistance and high resistance, respectively. This spin-valve effect allows one to explain the LFMR based on electron flow across GBs and/or inter-grain amorphous phases in polycrystalline manganites (figure 4(b)). A moderate external magnetic field can suppress the spin fluctuations and align grain magnetizations randomly oriented at zero-field. As a result, the resistivity drops and a negative MR is observed, which depends critically on the spin states in the neighbouring magnetic regions and field-induced rotation of the magnetic domains as well as GBs features, occurring of magnetic inter-grain zones and extension of canted spin regions. As a result, the magnetic domain structure of polycrystalline specimens has been extensively studied using different microscopic tools [61-62]. Whereas polycrystalline films have a significantly higher resistivity than their epitaxial counterpart, LFMR in the perovskite manganites La_{1-x}A_{x}MnO_3 with A = Sr, Ca, Ba, and Pb has been emphasized from the point of view of potential applications in digital recording and sensing industries [11, 53, 63].

![Figure 4:](image)
3. LSMO thin films by PLD and influence of growth conditions

LSMO intriguing properties are strongly related to the lattice-charge-spin coupling, which is very sensitive to phase/structural transformations, oxygen stoichiometry, growth temperature and lattice distortions induced by doping.

Pulsed laser deposition is an ablation technique based on non-equilibrium laser-matter interaction that experienced a rapid spread since 1987 when it revealed very successfully to deposit thin films of high critical temperature superconductors [64]. A crucial advantage of PLD consists of its ability to “transfer” the stoichiometry of complex multi-elemental targets on different substrates. Figure 5 depicts a typical PLD experimental set-up. A short and high-energy laser pulse is focused on a highly absorbing target material. The resulting intense localized heating induces an increase of the local temperature and an instantaneous vaporization/ejection of all the target elements with ionization and formation of a plasma plume. The underlying non equilibrium laser-matter interaction is a process quite different from thermal evaporation where composition depends on the vapour pressures of elements in the target material. In PLD approach, after ablation, plasma species are transferred to the substrate by strongly forward-directed expansion in a controlled background atmosphere [20, 21]. In this respect, ablation can take place either in vacuum or in an inert or reactive atmosphere (reactive PLD) and ambient gas parameters can be tuned to determine the interaction processes and dynamics of the ablated species. For this reason, PLD is the most versatile method for tuning both rate and kinetic energy distribution of the deposition flux [22]. Since growth is driven by periodic bursts of energetic species deposited on a substrate, ad-atoms interact with the growing surface differently from the case of thermal deposition [23]. This allows effective diffusivity regime even at low substrate temperatures, high adhesion to the substrate, epitaxial growth at lower temperature compared to other deposition methods, transition among growth modes, and promotion of the nucleation rate due to the supersaturation and tunable repetition rate of the deposition flux [22, 23]. All these factors are important for the optimal grow of complex materials which, additionally, are sensitive to structural and phase transformations as well as to improve the structural quality and promote very smooth interfaces, which is a basic prerequisite to design functional spin-tunnelling devices.

For LSMO target ablation, basically different laser sources were employed, however, most of them belong to the class of the excimer lasers and the most used are frequency-tripled Nd:YAG laser, KrF (248 nm) or ArF excimer lasers (193nm). Optimal fluence and pulse repetition rate depend on the perovskite oxide to be grown, dopant, substrate nature and deposition temperature. Fluence values

![Figure 5: Schematic representation of a standard PLD experimental set-up.](image)
around 4J/cm² and 1.5 J/cm² are reported in the case of ArF and KrF lasers, respectively, while ablation with Nd:YAG laser is typically performed at 8.5 J/cm² for room temperature deposition and at 3 J/cm² or lower at higher temperatures. Usual repetition rates range between 5-10 Hz. Reducing the deposition flux frequency favours collisions between oxygen species and ad-atoms migrating on the growing film in between subsequent laser pulses. High deposition temperatures (higher than 600°C) and post-deposition annealing and/or cooling procedures down to room temperature under controlled oxygen pressures are generally mandatory to stabilize structural order, according to the LSMO phase diagram, and obtain maximum MR [38, 54, 56, 65-70]. Raising the substrate temperature provides a driving force for a more effective migration of the adsorbed species, increases the collision rate and nucleation probability and promotes the onset of crystalline phases. However the substrate thermal response plays an important role in determining the maximum allowed as well as the effective growth temperature. Additionally, substrate temperature influences the film oxygen content through oxygen desorption rate. Different parametric studies on the influence of the oxygen pressure on the film magneto-electrical properties are reported in literature but the most used values are around 100 mTorr or 200 mTorr.

Since spintronic applications require $T_c$ and $T_{MI}$ above room temperature, the challenge is to increase both critical temperatures by tuning the deposition parameters. For bulk single crystals and high quality epitaxial films $T_{MI}$ is very close to $T_c$ [36]. On the contrary, in polycrystalline LSMO, $T_{MI}$ is much lower and reducing/oxidizing growth atmospheres result in decreased/increased critical temperatures [71, 72]. The $T_{MI} < T_c$ obtained for granular films has been related to the presence of structural defects and GB regions and depends on growth conditions [73-75]. A $T_{MI} > T_c$ has been also observed in the case of crystalline LSMO films grown by metallicorganic chemical vapour deposition [76]. Definitively, whereas no general link can be established between the two critical temperatures, their relationship and separation can be tuned by growth conditions promoting structural order. In this respect, in order to investigate the correlation between $T_{MI}$ and $T_c$, microstructure, strain and lattice order must be taken into account. As an instance, substrate material, growth temperature and film thickness can induce Curie temperature shift by lattice strain and modified growth kinetics. Basically strain is a function of lattice and thermal expansion mismatch between film and substrate and can lead to distortion and/or rotation of the MnO$_6$ octahedron. There has been particular interest in the electronic transport and CMR effects of thin films owing to the interplay between substrate-induced strain on the overlayer structure and film thickness [77-79]. In this respect, epitaxial strain imposed by the substrate is an additional degree of freedom for tuning functional properties [80-84]. It has been reported that LSMO thin films epitaxially grown on SrTiO$_3$(001) by PLD can exhibit relatively high room temperature magnetization and $T_{MI} > T_c$ while LSMO films grown onto MgO(001) were found to exhibit nearly equal high critical temperatures. In addition sizable critical temperatures were demonstrated by changing the laser pulse repetition rate and the growth temperature [38]. In this respect, it has been obtained that (i) reducing the former parameter (from 3.3 Hz to 1.3 Hz) at constant substrate temperature (660°C) causes the Curie temperature $T_c$ to increase from 305 K to 340 K, and (ii) increasing the substrate temperature up to 730 °C keeping the repetition rate at 1.3 Hz increases $T_c$ to 350 K.

LSMO deposition by PLD was reported on very different and differently oriented substrates, namely (001) and (100) SrTiO$_3$(STO), (001) and (100) LaAlO$_3$(LAO), YAlO$_3$(YAO), (001)-oriented (LaAlO$_3$)$_0.9$(Sr$_2$AlTaO$_6$)$_{0.1}$ (LSAT), (110)-oriented DyScO$_3$ (DSO), GdScO$_3$ (GSO), NdGaO$_3$ (NGO) with orientations (100), (010), (110) and (001), (001) LaSrGaO$_4$(LSGO), (100) Y-stabilized ZrO$_2$ (YSZ), piezoelectric Pb(Mg$_{1/3}$Nb$_{2/3}$)$_{0.72}$Ti$_{0.28}$O$_3$, crystalline substrates with buffer layers, (001) and (100) MgO, (100) GaAs, (100) Si and amorphous quartz [80, 81, 84, 85-91]. For films epitaxially grown on crystalline substrates, deviations from the bulk lattice constant are observed, depending on the substrate lattice constant and orientation [92]. Substrate-induced stress leads to strong structural variations of the LSMO unit cell influencing the magnetic microstructure of LSMO films which is correlated to the easy axis of magnetization. For example, Kwon et al. [80] reported an in-plane easy magnetization direction in tensile-strained films grown on STO(001) substrates and an out-of-plane
easy axis in compressively strained films grown on LAO(001) substrates. Furthermore, the magnitude of the tetragonal distortion depends on the relative film–substrate crystallographic orientation with differences observed in both mean grain diameter and film roughness [93, 94].

A gradual change of the grain texture with the substrate temperature during deposition was reported for polycrystalline LSMO films grown on YSZ(100) substrates by PLD with substrate temperature ranging from 600 to 850 °C [72]. Another important aspect is the adatom mobility during the growth on different substrates. The observed similarity in film surface morphology independently from the substrate considered means that during ablation, the good superficial migration allowed by PLD favours both optimal adhesion between film and substrate and strains to be accommodated leading to strong relaxation/distortion of the lattice cell. While for large mismatched MgO substrates the biaxial stress relaxes in a layer of few nanometers, on GaAs lattice mismatch and inter-diffusion make necessary an epitaxial buffer layer but substrate temperature during its deposition should not exceed ~550°C due to threatening decomposition of GaAs. As a consequence, the choice of the buffer-layer material is limited and for this reason MgO is generally employed as buffer layer because it does not require very high deposition temperatures to grow epitaxially and it has better diffusion barrier properties compared with other materials like YSZ. Epitaxial LSMO thin films can be grown on lattice-matched substrates as well as on Si by using lattice-matched buffer layers such as STO, YZS. On the other hand, polycrystalline LSMO films on Si substrates can be obtained by allowing the LSMO to grow on an oxide coating. In this case, growth temperatures below 500°C are considered to allow the preliminary formation of the native oxide on the Si surface. Quartz wafer were also employed as substrate with the aim to avoid the potential effect of crystalline substrates on the film orientation by minimizing the stress effects resulting from epitaxial growth on crystalline substrates.

Another very critical parameter in determining LSMO magnetic and electrical properties is oxygen stoichiometry [72, 85, 95-98]. Basically, each lost oxygen leads to the conversion of two Mn$^{4+}$ ions to Mn$^{3+}$ ions, causing irregular octahedral coordination for Mn atoms and weakening of Mn-O-Mn bondings by lattice expansion. As a consequence, oxygen vacancies strongly reduce carrier density, introduce lattice structural disorder that partially localizes carriers, weaken the DE charge-transfer mechanism through Mn-O-Mn oxygen bridges, decrease both critical temperatures $T_{MI}$ and $T_{C}$ and increase material resistivity. In contrast, oxidizing conditions lead to ferromagnetic-metallic phase extending up to higher temperatures, due to an increased hole concentration induced by cation vacancies and a decreased Mn-O average distance and the increased Mn-O-Mn bond angles which favour DE. Oxygen stoichiometry depends on growth oxygen pressure, substrate temperature and background atmosphere during post-deposition cooling treatments. Oxygen desorbs from doped manganites at elevated growth temperatures, in a reducing atmosphere as well as during cooling procedures in vacuum. According to the defect model by Roosemalen, under some oxygen partial pressure the excess oxygen concentration decreases with increasing annealing temperature, while at definite annealing temperature the excess oxygen concentration increases with increasing oxygen partial pressure [99-101]. Importantly, oxygen vacancies do not involve irreversible structural disorder: oxygen can be introduced into the sample by annealing the film at high temperatures (~ 400-600°C) in an oxygen-rich atmosphere. When control on oxygen content is desired, PLD is a very versatile technique because increasing the oxygen pressure or reducing the laser frequency during deposition are equivalent ways to promote collisions between oxygen species and the growing film [38, 98].

Finally, the substrate temperature is also important in influencing the film microstructure and, consequently, the film magnetic and electric properties. While thin films grown at low temperature show amorphous or mixed amorphous/nanocrystalline microstructure, the ones growth at temperature higher than 600°C allows improved crystalline order [102]. Generally for thin films raising the substrate temperature involves a gradual evolution from the PM state to the FM one as well as a crossover from the insulating mode to the metal-like one. This is the result of the increased structural order which stabilizes the ferromagnetic and conductive behaviours.
4. LSMO-based devices: from Spintronics to Organic Spintronics

Spintronics emerged with the discovery of giant magnetoresistance (GMR) by Fert and Grünberg [103, 104] who received the Nobel Prize in Physics in 2007. In magnetic tunnel junctions, the nonmagnetic spacer consists of a thin insulating layer and the MR effect is referred to as tunnel magnetoresistance (TMR). In TMR structures, given the spin conservation during tunneling, the tunnel rate is proportional to the product of the corresponding spin subband DOS at the Fermi level [3]. As a consequence, half-metal LSMO is an optimal material for magnetic tunnel junctions [26]. Moreover, LSMO is very attractive since the conductivity mismatch problem for direct spin-polarized injection at the ferromagnetic metal-semiconductor interface does not apply to fully spin-polarized systems. LSMO has also proved to be a successful spin-injector in artificial grain-boundary devices [105].

The discovery of TMR and GMR in metallic spin-valves meant a revolution in magnetic memories. Very recently the introduction of hybrid spintronic devices consisting of organic materials and conventional magnetic electrodes were another promising turning-point. Organic materials are very appealing because weak spin-orbit and hyperfine interactions in molecules make the spin-relaxation and spin coherence times very long [106]. In organic spintronic devices, organic materials are usually used to decouple two ferromagnetic electrodes while mediating or controlling a spin-polarized signal injected and collected by the ferromagnetic contacts. Relevantly, in this new field, LSMO is the most widely used ferromagnetic spin-injection contact, starting from the first proposed organic spintronic device: an OLED structure consisting of planar LSMO electrodes separated by a nearly 100 nm long channel of α-sexithiophene [107]. In this respect, the low conductivity of LSMO allows to minimize the conductivity mismatch with the organic semiconductor.

Concerning spin valves, prototype hybrid structures based on LSMO and organic semiconductors have been demonstrated [28, 108]. The first functional organic spin-valve [28] consisted of LSMO and Co FM electrodes sandwiching a thick (100-200nm) tris(8-hydroxyquinolinato)aluminium (briefly termed Alq3) nonmagnetic layer. Figure 6(a) shows the sketch of this large scale vertical device and the bias circuit configuration. The arrow indicates the applied external in-plane magnetic field. Figure 6(b) is a scanning electron micrograph of a LSMO/Alq3/Co/Al functional spin-valve device. Then, the measured MR response is reported in figure 6(c): the relative magnetization directions of the ferromagnetic electrodes are indicated by horizontal arrows and the sweep direction is shown by the vertical arrows. LSMO spin-injection electrode and Co spin-detector electrode are used as soft and hard magnetic layers. Their different coercitive fields allow one to switch the relative magnetization directions of the ferromagnetic electrodes between parallel and antiparallel alignments, upon sweeping the applied magnetic field. Unlike standard spin-valve devices, the device exhibited lower resistance in the anti-parallel configuration of the electrode magnetizations and this inverse spin-valve effect was attributed to the negative spin polarization of the Co d-band (with a smaller density of states at the Fermi level for the majority spin than for the minority spin subband). An up to 40% negative GMR effect was measured at low temperature (11K). For increasing temperature the MR strongly decreased and such finding was ascribed not to a decreased spin-polarization of LSMO electrodes but to a reduced spin diffusion length.

The same electrodes LSMO and Co have also been used with other organic semiconductors [108]. In this respect figure 6(d) shows a MR loop at low magnetic field measured on a LSMO/CVB/Co spin-valve device at T=14K and with bias voltage of nearly 10mV positively applied to the LSMO electrode. CVB molecule, or 4,4-bis-(ethyl-3-carbazovinylene)-1,1-biphenyl, is an emissive oligomer. Again the device electrical resistance in the case of anti-parallel magnetizations is smaller as compared to the parallel configuration. Switching of the device resistance was confirmed to occur in agreement with the coercitive fields of the LSMO and Co electrodes, namely 500e and 6000e, respectively. The MR value at low magnetic field (<1kG), as estimated by the MR response in figure 6(d), was about 11%. Moreover, a monotonically MR decrease with increasing voltage V was reported.
Occurrence of inverse spin-valve effect gave rise to confusion and controversy concerning the sign and mechanisms of MR. Very recently a model invoking the formation of spin-hybridization–induced polarized states in the first molecular layer at the electrode interface has been proposed to explain the observed discrepancies on the MR signs in LSMO/Alq3/Co spin valves [109].

Room temperature MR in LSMO/Alq3/Al2O3/Co devices was demonstrated [110] by improving the quality of both injecting interfaces. Although the observed MR was quite weak, in this case it decreased with temperature in agreement with the surface magnetization of the LSMO and vanished at its Curie temperature [108]. Therefore, the thermal response of LSMO/Co-based spin-valve devices critically depends on the LSMO–interfacial spin-polarization value that vanishes at lower temperature (nearly 220K) compared to the bulk magnetization.

The possibility to inject and transfer spin-polarized currents within carbon nanotubes (CNTs) in a LSMO-CNT-LSMO structure was also demonstrated, along with the transformation of spin information in large electrical signals thanks to the large spin lifetime and mean electron velocity in the channel resulting in large MR [111]. Figure 7(a) and 7(b) show the structure of the junction fabricated by photolithography with LSMO electrodes deposited on lattice matched NdGaO3 substrates and having a 1.5 µm separation and a variable width (1-4 µm, to switch independently their magnetizations). The authors reported tunnel junction-like characteristics and a maximum MR ratio around 60% at 5K (figure 7(d)) with a bias voltage of 25mV, which decreased at larger temperatures until vanishing at 120K (figure 7(e)).
Very recently, LSMO/C$_{60}$ spin valves have been also implemented. Indeed, devices based on fullerene C$_{60}$ spacer layer are expected to possess thermal stability, namely improved signal/noise ratio of the MR loop measurement [112]. Moreover, while the abundant hydrogen atoms in most organic materials increase the hyperfine coupling, in carbon such coupling occurs only in the rare $^{13}$C carbon isotope. Therefore the weak hyperfine interaction of the C$_{60}$ molecule may increase spin lifetimes in organic spin valves based on fullerene.

5. Summary

In summary, the LSMO fundamental magneto-electro-optical properties have been outlined and discussed with respect to their dependence on the deposition parameters and conditions. LSMO has been considered due to its rich physics determined by interplay between charge, lattice and spin interactions. For this reason it is a very interesting material for applications, even in the new field of organic spintronics. Since LSMO structural and magnetic order is very sensitive to the deposition technique, PLD is a very powerful tool to growth high quality films and favour ferromagnetic and conductive phases. In this respect, different independent deposition parameters, namely oxygen pressure, laser fluence and repetition rate, substrate temperature and post deposition treatments, have been discussed concerning their influence on the LSMO properties through the film structure. It has been demonstrated that PLD let the growth of LSMO films with good and very well tailored properties to be used in selected applications.
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