Pulsed laser deposition of La$_{1-x}$Sr$_x$MnO$_3$: thin-film properties and spintronic applications

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Abstract
Materials engineering on the nanoscale by precise control of growth parameters can lead to many unusual and fascinating physical properties. The development of pulsed laser deposition (PLD) 25 years ago has enabled atomistic control of thin films and interfaces and as such it has contributed significantly to advances in fundamental material science. One application area is the research field of spintronics, which requires optimized nanomaterials for the generation and transport of spin-polarized carriers. The mixed-valence manganite La$_{1-x}$Sr$_x$MnO$_3$ (LSMO) is an interesting material for spintronics due to its intrinsic magnetoresistance properties, electric-field tunable metal–insulator transitions, and half-metallic band structure. Studies on LSMO thin-film growth by PLD show that the deposition temperature, oxygen pressure, laser fluence, strain due to substrate–film lattice mismatch and post-deposition annealing conditions significantly influence the magnetic and electrical transport properties of LSMO. For spintronic structures, robust ferromagnetic exchange interactions and metallic conductivity are desirable properties. In this paper, we review the physics of LSMO thin films and the important role that PLD played in advancing the field of LSMO-based spintronics. Some specific application areas including magnetic tunnel junctions, multiferroic tunnel junctions and organic spintronic devices are highlighted, and the advantages, drawbacks and opportunities of PLD-grown LSMO for next-generation spintronic devices are discussed.

1. Introduction
The technology of spintronics uses the charge and spin of electrons to store information or to carry out logic operations [1, 2]. Spintronic components are often more versatile, energy efficient and faster than their conventional counterparts. Major developments in spintronics include giant magnetoresistance (GMR) [3] in metallic multi-layers and spin-valve devices, and tunnelling magnetoresistance (TMR) [4] in magnetic tunnel junctions (MTJs). Both effects have been used in commercial applications including magnetic field sensors, the read head of magnetic hard-disk drives and non-volatile magnetic random access memories (MRAMs). Many functional spintronic devices require a highly spin-polarized injector and detector. La$_{1-x}$Sr$_x$MnO$_3$ (LSMO) with $x = 0.2–0.4$ has been a popular choice as magnetic electrode in both inorganic and organic spin-based structures because of its fully spin-polarized conduction band at the Fermi level [5]. Other interesting properties of LSMO include a matching work function with several organic semiconductors (OSs) and polymers and a metal–insulator transition that is tunable by lattice strain and electric fields.

Pulsed laser deposition (PLD) [6] is a versatile thin-film deposition technique that can be used for nanoscale engineering of complex materials and interfaces. In correlated electron systems such as LSMO, strong lattice–charge–spin coupling offers extensive control of magnetic and electronic transport properties by growth optimization and external actuation [7]. In addition to intrinsic material parameters, spintronic elements often rely on band-structure effects at
rare-earth La$^{3+}$ ions are the largest, while the smaller Mn ions and dopant cations, the tolerance factor on the radius of the LSMO is determined by charge neutrality, which also depends on the radius of the A-site dopant (Sr). In the LSMO lattice, the rare-earth La$^{3+}$ ions are the largest, while the smaller Mn ions exhibit the mixed-valence phase of Mn$^{3+}$ and Mn$^{4+}$, depending on the hole doping concentration $x$.

The electronic properties of LSMO are strongly correlated with the crystal structure. In an ideal perovskite structure, the five d orbitals of an isolated Mn ion undergo a crystal field splitting into a $t_{2g}$ triplet (consisting of the $d_{x^2}$, $d_{y^2}$, and $d_{z^2}$ orbitals) and an $e_g$ doublet (originating from the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals) as schematically shown in figure 2. The degeneracy of the levels is further lifted by lattice distortions that lower the crystal symmetry, also known as Jahn–Teller (JT) distortions. Due to the tetragonal distortion of the MnO$_6$ octahedra the $t_{2g}$ triplet is energetically lower than the $e_g$ doublet. Lifting of the two-fold degeneracy of the $e_g$ spin-up and spin-down bands by JT distortions results in the spin-resolved band structure of LSMO [5]. Therefore, 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 a higher lying $e_g$ state (with crystal field splitting $\Delta \approx 1.5$ eV between the lowest $t_{2g}$ and the highest $e_g$ level). As substitution of each trivalent La$^{3+}$ by divalent Sr$^{2+}$ in LaMnO$_3$ induces itinerant holes, a doping concentration of $x = 0.3$–0.4 leads to a roughly equal number of Mn$^{3+}$ and Mn$^{4+}$. Depending on the doping concentration, LSMO has a conduction band that is either more ($x < 0.5$) or less ($x > 0.5$) than half-filled. In hole-doped LSMO ($x < 0.5$), the fully occupied spin-up localized $t_{2g}$ band and partially occupied spin-up $e_g$ band are separated from the empty minority bands by a large Hund’s energy of about 2.5 eV. For both spin orientations, the oxygen 2p states are fully occupied and the electronic structure near the Fermi level is determined by hybridization between the majority spin Mn-$e_g$ states and the O-p states. The minority spin states and the O-2p band are separated by an insulating band gap and therefore only majority carriers are present at the Fermi level, i.e. LSMO is a half-metal for $x = 0.3$–0.4. The 100% spin polarization at the Fermi level of LSMO is much larger compared with the $\approx 40\%$ spin polarization of ferromagnetic 3d transition metals [10–13].

The phase diagram of mixed-valence LSMO [7, 14] is shown in figure 3. For low hole doping ($x < 0.1$), LSMO is an antiferromagnetic insulator (AFM-I). With increasing hole doping, first a ferromagnetic insulating (FI-M) ($x < 0.2$) and eventually a ferromagnetic metallic (FM-M) ($x = 0.2$–0.4) ground state are stabilized. For $x = 0.3$, a metal–insulator transition is observed at $T_{MI}$, which is close to $T_C$.

Both the metal–insulator and the paramagnetic–ferromagnetic phase transitions are connected to the electronic distribution of spin-up and spin-down states and the width of the impurity band. The magnetic and transport properties in this correlated electron system are essentially influenced by the size of the $A$-site cations which controls the tolerance factor, the average Mn–O bond length, and the Mn–O–Mn bond angle of the MnO$_6$ octahedra. The two transition temperatures $T_{MI}$ and $T_C$ can either coincide (for single crystals or epitaxial thin films) or vary substantially depending on the presence of structural defects and grain boundaries.

The regime in which ferromagnetism and metallic conduction coexist is generally explained by double exchange (DE) [15, 16] between localized 3d magnetic moments with...
Figure 2. (a) Crystal field splitting of the Mn ion d-levels and electronic occupation of the mixed-valence Mn ions. The degeneracy of the eg and t2g levels is lifted by an in-plane contraction and out-of-plane elongation of the oxygen octahedron. (b) Schematic illustration of the density of states of LSMO and Ni showing the fully spin-polarized conduction band of LSMO. Adapted from [7] and [32].

Figure 3. Phase diagram of La$_{1-x}$Sr$_x$MnO$_3$, reproduced with permission from [14].

strong on-site Hund’s coupling. Hopping of eg electrons between adjacent Mn$^{3+}$ and Mn$^{4+}$ along the Mn–O–Mn chains governs both ferromagnetism and metallic transport. The hopping probability is largest when the Mn spins are aligned parallel. Anderson and Hasegawa have shown that the transfer integral varies as the cosine of the angle between neighbouring spins [17]. Hence, charge carriers can move easily in the ferromagnetic phase while they get localized due to randomly aligned Mn spins when the manganite is paramagnetic. Mechanisms that are capable of modifying the spin alignment, such as magnetic field or temperature, can therefore alter the carrier mobility and the resulting electrical conductivity. With decreasing temperature, the combined itinerant and local-moment system lowers its total energy by ferromagnetic spin alignment and by allowing the itinerant electrons to gain kinetic energy [18]. However, Millis et al [19–21] have shown that a Hamiltonian incorporating the DE interaction alone cannot explain CMR in manganites [7]. It was proposed that in addition to DE, an electron–phonon coupling term dictates electronic transport, which is expected for a system where electrons hop between Mn$^{3+}$ and Mn$^{4+}$ ions. Hole doping of the system replaces Mn$^{3+}$(d$^4$) by Mn$^{4+}$(d$^3$) which, in the dilute limit, is associated with large JT coupling. The DE model with the inclusion of JT distortions explains the CMR effect and the high-temperature paramagnetic phase in LSMO and other manganites in general.

In LSMO, different MR mechanisms are active including CMR and low-field magnetoresistance (LFMR). CMR is associated with the suppression of spin fluctuations in an applied magnetic field and therefore a fairly large magnetic field (a few tesla) is required [7]. LFMR is due to the suppression of spin-dependent scattering at grain boundaries or tunnelling between grains, which requires a small magnetic field that is comparable to the coercivity [22]. In the low-temperature ferromagnetic phase (below $T_C$), the conduction electrons are almost completely polarized inside a magnetic domain resulting in easy transfer of electrons within the Mn–O–Mn chains. Hence, in single crystals or epitaxial thin films the manganite resistance does not change substantially in a small applied magnetic field. However, for polycrystalline bulk materials or thin films, the differently aligned magnetic domains and the grain boundaries can act as insulating scattering centres for spin-polarized electrons, which enhances the zero-field resistivity. There are two different effects related to LFMR. (i) Electrons from one magnetic domain hop to another magnetic domain through an intermediate insulating layer by a spin-dependent tunnelling process (<500 mT) and (ii) suppression of spin fluctuations at grain boundaries at larger fields (>500 mT). The probability of spin-dependent tunnelling depends strongly on the spin states of neighbouring grains. At the coercive field, half of the domains switch their magnetic orientation. Hence, the tunnelling probability of electrons is the smallest at $H_c$ and the electrical resistance peaks. After successive magnetization reversal into the direction of the external magnetic field, the tunnelling probability again increases leading to a decrease of the electrical resistance. There are reports of up to 20% LFMR in polycrystalline LSMO thin films on single-crystal (001)
scattering on impurities, defects, domain walls and grain boundaries. The low-temperature ferromagnetic phase, the resistivity of LSMO has been fitted with equations of the form [24]

$$\rho = \rho_0 + \rho_2 T^2$$  \hspace{1cm} (1)

$$\rho = \rho_0 + \rho_{2.5} T^{2.5}$$  \hspace{1cm} (2)

$$\rho = \rho_0 + \rho_2 T^2 + \rho_{4.5} T^{4.5}$$  \hspace{1cm} (3)

where $\rho_0$ is the resistivity due to temperature-independent scattering on impurities, defects, domain walls and grain boundaries. Generally, $\rho_0$ decreases significantly in an applied magnetic field due to an improved spin alignment at grain boundaries and domain walls. The temperature dependence of the resistivity originates from different scattering sources. For example, Urushibara et al. [24] showed that the resistivity of single-crystal LSMO can be fitted well below 200 K using equation (1). In this case, the $T^2$ term predominantly accounts for electron–electron scattering. Additional electron–magnon scattering can be taken into account by the introduction of a $\rho \propto T^{4.5}$ term (equation (3)), which is typical for DE systems ([18] and references therein). However, equation (2) provides a better fit to some experimental data. Finally, electron–phonon scattering does increase the resistivity of LSMO at high temperatures. Just like $\rho_0$, the temperature-dependent terms ($\rho_2, \rho_{2.5}$ or $\rho_{4.5}$) decrease in a magnetic field. Snyder et al. [25] suggested that the decrease in $\rho_2$ is proportional to $H^{-1/3}$, which implies that a reduction of spin fluctuations suppresses electron–electron scattering in LSMO.

3. Control of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ properties by PLD

PLD is a thin-film ablation technique based on laser–matter interactions. In a PLD setup, a short and high-energy laser pulse is focused on a target. The intense local heating induces ejection of target ions into a plasma plume. The substrate, placed at an optimum distance from the target, receives the plasma ions and under the right deposition conditions (temperature, background gas pressure, laser fluence and pulse repetition rate) high-quality films can be grown. The stoichiometry of complex multi-element materials is conserved during the PLD process. In addition, PLD is a powerful technique for obtaining smooth defect-free interfaces between thin films, which is of particular interest for spintronic structures.

The magnetic and electrical transport properties of LSMO are controlled by lattice–charge–spin coupling, which is very sensitive to phase and structural order, oxygen stoichiometry and lattice distortions induced by doping [26–28]. In thin films, the physical properties are further influenced by low- and high-angle grain boundaries (polycrystalline growth) and lattice strain. For PLD of LSMO thin films, mainly excimer lasers (Nd : YAG laser, KrF (248 nm) and ArF (193 nm)) are used. The laser fluence and pulse repetition rate for optimal LSMO films depend on the composition, substrate and deposition temperature. High deposition temperatures (>650 °C) and post-deposition annealing under a controlled oxygen pressure are generally required for the growth of high-quality LSMO films. Although the optimum deposition parameters vary for films grown by different groups, typical growth parameters for LSMO thin films are a deposition temperature of 700–800 °C, an oxygen pressure of about 0.25 Torr, a laser repetition rate of 5–10 Hz and a laser fluence of 2–2.5 J cm$^{-2}$.

For spintronic applications, the large spin polarization of LSMO is a desirable property. In addition, a high $T_C$, good metallic conductivity and atomically smooth interfaces are often essential for practical devices. Because strain control in thin LSMO films is vital for obtaining optimal properties, the effects of strain have been studied extensively [29–31]. More details can, for example, be found in [32] and references therein. Various single-crystal substrates including SrTiO$_3$ (STO), LaAlO$_3$ (LAO), NdGaO$_3$ (NGO) and MgO have been used for PLD of LSMO. Because of the small lattice mismatch between LSMO and these substrates (except for MgO), the lattice strain is not released easily. For example, 20–30 nm thick LSMO films on STO are still considerably strained and bulk-like lattice parameters are only obtained for considerably thicker films. The MnO$_6$ octahedra of strained LSMO are distorted and the hopping probabilities of $e_g$ electrons are restricted. Localization of $e_g$ electrons reduces the ferromagnetic interactions and it enhances the electrical resistivity of thin LSMO films, two effects that are not desirable for spintronic structures.

Other factors that control the magnetic and electrical transport properties of LSMO are film composition, oxygen stoichiometry and crystal orientation [33–37]. The composition and oxygen content mainly affect the saturation moment and the transition temperature, whereas lattice strain and film texture can also induce magnetic anisotropy [38, 39]. Moreover, LSMO films with a polycrystalline texture can exhibit large LFMR and a large dielectric constant due to the presence of high- and low-angle grain boundaries.

To illustrate the influence of substrate selection and PLD parameters on the structural, magnetic and electrical properties of LSMO films, we discuss some of our results below [40, 41]. In the experiments, the LSMO films were systematically grown on three different single-crystal substrates (STO (0 0 1), NGO (0 0 1), MgO (0 0 1)) under a variety of PLD conditions. X-ray diffraction pole figures ($\varphi$–$\psi$ scans) of the (1 1 0) reflection at $2\theta = 32.76^\circ$ are shown in figure 4. Obviously, different crystal orientations are obtained in most of the samples. Only the films grown at 700 °C (indicated by number 5) and a LSMO thickness of about 200 nm on MgO and STO are fully epitaxial. All other films contain additional crystal orientations with pseudocubic axes at 10°, 13°, 16° and 27° angles with respect to the substrate [0 0 1] direction. In addition, the reflections from LSMO films on MgO are much wider than those from STO and NGO samples, indicating the presence of low-angle grain boundaries with single grain orientation.

Magnetic measurements on LSMO/MgO (0 0 1) clearly indicate that the ferromagnetic–paramagnetic phase transition of LSMO is considerably broader than that of comparable films.
Figure 4. X-ray diffraction pole figures of the LSMO (1 1 0) reflection at $2\theta = 32.76^\circ$ on MgO, STO and NGO substrates with a (0 0 1) orientation. The PLD parameters for samples indicated by No 1 are growth temperature $T_S = 780^\circ C$, laser pulse frequency $f = 5$ Hz, and LSMO film thickness $t = 400$ nm. For 2, $T_S = 780^\circ C$, $f = 5$ Hz and $t = 200$ nm. For 3, $T_S = 780^\circ C$, $f = 10$ Hz and $t = 400$ nm. For 4, $T_S = 780^\circ C$, $f = 10$ Hz and $t = 500$ nm. For 5, $T_S = 700^\circ C$, $f = 10$ Hz and $t = 200$ nm. Reprinted from [40], Majumdar S et al. 2012 Stress and defect induced enhanced low field MR and dielectric constant in La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films 512 332, © (2012), with permission from Elsevier.

Figure 5. Temperature dependence of field cooled magnetization (left) and sheet resistance of LSMO films (right) on MgO, STO and NGO substrates grown under the same experimental conditions as sample 3 in figure 4. Adapted from [42].

on STO and NGO (figure 5). The broadening of the magnetic transition is accompanied by a metal–insulator transition at a temperature well below $T_C$. Both effects are explained by the formation of (0 0 1) and (2 1 1)-oriented grains during PLD of LSMO on MgO [41]. For LSMO films on STO and NGO substrates, the magnetic properties do depend less on the PLD growth conditions and film thickness, although the $T_C$ of 200 nm films on STO (342 K) is approximately 10 K less than for 400 nm films. The reduction in $T_C$ is ascribed to compressive film strain. The largest LFMR effect (17%) is obtained for the thickest LSMO film on MgO while the LFMR is only 1% for epitaxial films on STO and nearly epitaxial films on NGO. These results indicate that tunnelling through grain boundaries contributes significantly to the conduction of polycrystalline LSMO films on MgO. Finally, LSMO films on MgO (0 0 1) with a high density of grain boundaries possess a large dielectric constant ($\varepsilon'_r$) [40, 41]. At room temperature, $\varepsilon'_r$ remains large up to a frequency of a few kHz. This behaviour is explained by a variation of the conductivity and capacitance of grains and grain boundaries, which leads to Maxwell–Wagner-type polarization and the formation of a Schottky barrier at the interface. $\varepsilon'_r$ of epitaxial LSMO films on STO (0 0 1), on the other hand, remains relatively constant up to MHz frequencies. In this system, lattice strain mainly influences the evolution of $\varepsilon'_r$.

The coexistence of ferromagnetism with defect-induced LFMR and a large dielectric constant opens up new routes for a variety of interesting applications. For spintronics, however, epitaxial and defect-free LSMO films on lattice-matched substrates are more desirable. One drawback of LSMO-based spintronic structures is the relatively low $T_C$. Although the $T_C$ of LSMO thin films is about 360 K, it has been reported that it already starts to lose its spin polarization at $\approx 200$ K [43], especially near the surface of the LSMO film. Consequently, only a current with small spin polarization can be generated in LSMO-based spintronic devices at room temperature, which poses a serious challenge for practical applications. Also, the TMR of MTJs with LSMO electrodes is often smaller than expected, which suggests...
that the LSMO interface layer is not fully spin-polarized at the Fermi level. The reduction of spin polarization might be due to LSMO–tunnel barrier interactions. In fact, some studies indicate that LSMO can lose its half-metallicity in contact with a STO (0 0 1) substrate [44, 45]. According to polar discontinuity theory [46, 47], LSMO is composed of alternating SrO and TiO2 planes while (0 0 1)-oriented LSMO is deposited as alternating layers of (La0.67Sr0.33O)0.67+ and (MnO2)0.67−. Thus, the LSMO layers are charged while STO is charge-neutral. The polar discontinuity that occurs at the STO–LSMO interface leads to an electronic redistribution, which either reduces or enhances the charge carrier density in the interfacial layers of LSMO. As a result, the population of the e-g orbitals changes and via the DE mechanism this can alter the electrical conductivity and magnetic properties of the LSMO interface. To avoid detrimental effects due to polar discontinuities, interface engineering of LSMO–STO heterostructures has been suggested as a possible solution [48, 49].

One route towards interface engineering is based on the growth of LSMO films on substrates with different crystal orientations. For example, LSMO on (1 1 0)-oriented STO substrates exhibits a completely different interface structure from LSMO on STO (0 0 1) (figure 6). In the (1 1 0) system, the STO is composed of alternating SrTiO4+ and O4 planes. Since LSMO (1 1 0) contains alternating layers of La0.67Sr0.33MnO4+ and O2−, a polar discontinuity is avoided and the magnetization and spin polarization of the interfacial layers can be preserved. Experiments indeed show that (1 1 0)-oriented LSMO films possess a larger magnetic moment and higher Tc (increase of about 15 K) compared with (0 0 1)-oriented films [50]. Moreover, recent x-ray photoelectron spectroscopy (XPS) and high kinetic energy XPS studies indicate that LSMO films on STO (0 0 1) are under a larger tensile strain, due to strain effects in both the [1 0 0] and [0 1 0] in-plane directions. This not only affects the LSMO lattice parameters but also the angle between the unit cell axes. For (1 1 0)-oriented LSMO, strain effects along the [0 0 1] and [1 1 0] in-plane directions affect the LSMO lattice parameters. For (1 1 0)-oriented LSMO, the strain effect on the LSMO unit cell less. As a result, LSMO (1 1 0) films are more relaxed. This in turn leads to a smaller distortion of the MnO6 octahedra and a higher population of Mn4+ ions, which via improved DE interactions enhances the magnetic properties of LSMO.

4. Applications of La1−xSrxMnO3 in spintronics

4.1. Magnetic tunnel junctions (MTJs)

The ever-increasing demand for high-density magnetic data storage on computer hard-disk drives has motivated extensive research on MTJs that exhibit large TMR at room temperature. Moreover, MTJs form the storage cells in MRAMs. MTJs consist of a multilayer structure with two ferromagnetic electrodes that are separated by a thin insulating tunnel barrier. In most cases, dielectric oxides such as Al2O3 and MgO provide the necessary potential for quantum-mechanical tunnelling of electrons between the two ferromagnetic layers. The TMR effect is a measure of the relative change in tunnel barrier resistance upon magnetization reversal in one of the electrodes. The effect is largest when the alignment of the magnetic moments on either side of the tunnel barrier switches from parallel to antiparallel or vice versa. TMR originates from an imbalance between the number of majority and minority electrons that contribute to the tunnelling current. The spin-polarized band structure of the electrodes and spin filtering within the tunnel barrier can both contribute to the magnitude of TMR. When the influence of the tunnel barrier is negligible (e.g. for MTJs with amorphous Al2O3), the TMR effect is approximated by Julliere’s formula [51]:

\[
\text{TMR} = \frac{R_{AP}R_P}{R_{AP}} * 100\% = \frac{2P_1P_2}{1-P_1P_2}
\]

where \( R_{AP} \) and \( R_P \) are the tunnel barrier resistance for antiparallel and parallel aligned magnetic moments and \( P_1 \) and \( P_2 \) indicate the spin polarization of the electrodes. The latter quantity is often specified as

\[
P = \frac{N^\uparrow (E_F) - N^\downarrow (E_F)}{N^\uparrow (E_F) + N^\downarrow (E_F)}
\]

with \( N^\uparrow \) and \( N^\downarrow \) indicating the density of majority and minority electrons at the Fermi level.

Because of its half-metallic character, LSMO has been explored as an electrode material for MTJs (see for example [52, 53] for details). In most cases, the LSMO and barrier layers are grown by PLD. The first demonstration of TMR using LSMO electrodes was reported by a research group at IBM [54, 55]. The best results in this study were obtained using...
optimally doped La$_{2/3}$Sr$_{1/3}$MnO$_3$ electrodes and 3–6 nm thick STO tunnel barriers. The junctions, which were fabricated using a combination of optical lithography and ion-beam etching, showed a TMR of 83% at 4.2 K [54]. According to Julliere’s formula (equation (4)), this corresponds to a LSMO spin polarization of 54%. In subsequent years, considerably larger TMR values for LSMO-based MTJs were reported in the literature [56, 57]. For example, Bowen and co-workers reported a low-temperature TMR of 1850% for MTJs with a LSMO/STO/LSMO structure (figure 7) [56]. A spin polarization of 95% can be extracted from these experiments, which confirms the half-metallicity of LSMO.

Despite these promising results, LSMO electrodes exhibit some detrimental properties. In particular, the TMR effect of LSMO-based MTJs tends to decrease sharply with temperature, becoming negligible at room temperature [43]. Moreover, the MTJ resistance does not scale linearly with the inverse of the junction area [22], which suggests that electron tunnelling between LSMO electrodes is inhomogeneous. Finally, MTJs with LSMO electrodes often exhibit an irregular switching behaviour (figure 7). In the rest of this section, the temperature and bias voltage dependences of LSMO-based MTJs are briefly discussed. We also elaborate on the observation of inverse TMR effects and interface engineering strategies to overcome some of the drawbacks of LSMO.

**Temperature dependence.** Although LSMO-based MTJs often show very large TMR ratios at low temperatures, the effect decreases considerably at elevated temperatures irrespective of the tunnel barrier material [54, 58–60]. In particular, above $T \approx 200$ K, sharp decays of TMR are often observed [43]. Since this characteristic feature occurs well below the $T_C$ of LSMO films ($\approx 360$ K), it raises questions regarding the breakdown of half-metallicity. Polar discontinuity theory [46, 47] suggests the formation of a magnetically dead layer at the LSMO–STO interface, which is detrimental for the ferromagnetic properties and hence spin polarization of LSMO. In their study on LSMO-based MTJs with LAO and STO tunnel barriers, Garcia et al concluded that the spin polarization at the surface of LSMO decays much faster than that in the bulk due to the discontinuation of oxygen bonds [43]. In this picture, the distortion of the MnO$_6$ octahedra by dangling bonds acts as a localization centre for eg electrons and this results in a deterioration of the magnetic and electronic properties (figure 8). In experiments, the modified magnetic and electronic properties are often manifested by a decrease in $T_C$ and $T_{MI}$, a decrease in the saturation magnetization, and an increase in the resistivity and low-temperature magnetoresistance (MR). At LSMO–oxide barrier interfaces the oxygen bonds are better preserved and, hence, the interface spin polarization is considerably larger compared with that of free LSMO surfaces. However, both transport and spectroscopic studies indicate that even with better preserved oxygen bonds the spin polarization of the LSMO/oxide barrier interface vanishes completely at about 300 K. Large TMR values at room temperature remain therefore elusive for MTJs with LSMO electrodes.

**Bias voltage dependence.** Another striking feature of LSMO-based MTJs is a fast decay of the TMR effect with increasing bias voltage, especially in the low ($\leq 0.2$ V) bias range (figure 9) [61–63]. This strong bias dependence is accompanied by a zero-bias anomaly in the conductance curves. Gu et al theoretically studied the anomaly and they proposed that the tunnel barrier conductance is proportional to $|V|^{3/2}$ due to DE interactions in LSMO [64]. They showed that the stimulation of spin excitations, caused by strong Hund’s coupling between the conduction eg electrons and the localized quantum spins of the LSMO ions, assists electron tunnelling even for antiparallel aligned electrodes. As a result, an extra tunnelling conductance and a decrease in TMR are obtained. These findings are also confirmed by experimental studies [54, 63]. At a bias voltage of about 350 mV, a plateau in the TMR curve is generally observed, which is followed by another sharp decrease beyond 400 mV (figure 9) [63]. The
Inverse TMR. Depending on the choice of barrier material and the applied bias voltage, both normal and inverse TMR effects can be observed in LSMO-based MTJs. De Teresa et al. [68] showed that for a LSMO and Co electrode, normal TMR is observed for an Al2O3 (ALO) tunnel barrier while for STO and Ce0.69La0.31O3 (CLO) barriers the TMR response is inversed (figure 10). In the latter case, insertion of a thin ALO layer between the STO tunnel barrier and the Co electrode changes the sign of the TMR effect, but insertion of ALO between the STO barrier and LSMO does not alter the TMR response. These results are explained by a change in tunnelling spin polarization due to different types of bonding at the dielectric oxide–Co interfaces. The effective polarization of Co is negative for STO or CLO barriers, but positive for ALO. The negative tunnelling spin polarization of Co indicates preferential transmission of d electrons from the Co–STO and Co–CLO interfaces, while the positive polarization is due to predominant tunnelling of s electrons from the Co–ALO interface. Consequently, inverse and normal TMR effects are observed for tunnelling of d electrons and s electrons, respectively. Inverse TMR effects have also been observed in LSMO-based MTJs with a Co0.6Fe1.0 [69, 70], CoFeB [71] and Fe or Ni40Fe60 [72] counter electrode.

Interface engineering. Several interface engineering techniques have been explored to improve the performance of LSMO-based MTJs. Due to a polar discontinuity, a STO tunnel barrier donates holes to LSMO electrodes [73]. The insertion of two unit cells of LaMnO3 between LSMO and STO can compensate for the charge transfer at LSMO/STO interfaces [48]. Experiments indicate that the magnetic properties of this engineered interface are better; however, significant improvements of the TMR response and the temperature stability have not yet been demonstrated [49]. Other routes that have been explored include the use of LAO tunnel barriers [48] or the growth of more stable LSMO (1 1 0) electrodes [74]. Also in these cases, only limited enhancements of MTJ properties are obtained.

4.2. Multiferroic tunnel junctions (MFTJs)

One of the recent trends in spintronics is the exploration of electric-field-controlled magnetism. Materials that combine magnetic and ferroelectric phases, or so-called multiferroics, offer this desirable property via magneto-electric (ME) coupling between two ferroically ordered states. Unfortunately, single-phase multiferroic materials are rare and their application potential is often limited by low ordering temperatures, small ferroelectric polarization or magnetization, or weak ME coupling. As an alternative, studies on multiferroic heterostructures have greatly intensified in recent years (see e.g. [75, 76] for reviews). In a multiferroic heterostructure, magnetic and ferroelectric films are artificially assembled and the ME coupling originates from direct or indirect interactions at the interfaces. Each material constituent of a multiferroic heterostructure can be independently optimized for high-temperature operation, which facilitates their integration into practical devices. Moreover, since a wide variety of magnetic and ferroelectric materials are available, the nature and strength of ME interactions can be systematically altered and maximized. This has led to the engineering of large ME responses that exceed those of single-phase multiferroic materials by several orders of magnitude. Complex oxide materials are of particular interest for multiferroic heterostructures because their physical properties are very sensitive to external parameters including strain and electric fields. In fact, electric-field control of LSMO properties has been achieved by PLD growth onto piezoelectric substrates [77–81]. In these structures, an electrically activated piezostrain is transferred to the LSMO layer, which alters the magnetic and electrical transport properties. Direct electric-field effects have been obtained in systems where LSMO is directly coupled to a ferroelectric material. Here, out-of-plane polarization reversal in the ferroelectric causes charge accumulation or depletion in the interfacial layers of LSMO, which for an appropriately selected doping concentration x can lead to magnetic and electric phase transitions. Finally, LSMO has been used extensively as a bottom electrode in MFTJs. In this section, we will briefly review the physics of MFTJs and electric-field-controlled LSMO phase transitions.

MFTJs consist of two ferromagnetic electrodes separated by an insulating ferroelectric tunnel barrier. In most cases, the ferroelectric material is BaTiO3 (BTO), PbTiO3 (PTO) or...
Figure 10. TMR response of MTJs with a LSMO and Co electrode and a STO (a), CLO (b), ALO (c) or hybrid ALO/STO (d) tunnel barrier at 40 K. Reprinted with permission from [68]. Reprinted with permission from AAAS.

Figure 11. Evidence of ferroelectricity in 1 nm (left) and 3 nm (right) thick BTO films on LSMO. Reprinted by permission from [83], © (2009), Macmillan Publishers Ltd.

PbZr$_{0.2}$Ti$_{0.8}$O$_3$ (PZT). Tunnel junctions with a single-phase multiferroic tunnel barrier have also been studied [82]. In all junctions, PLD is used to grow the LSMO bottom electrode. In addition to the necessary electrical conductivity, LSMO provides a compressive lattice strain to the BTO, PTO or PZT tunnel barrier, which stabilizes the out-of-plane ferroelectric polarization. Using piezo-response force microscopy (PFM), Garcia et al have shown that the ferroelectric polarization of ultrathin BTO films on LSMO can be retained down to a film thickness of only 1 nm (figure 11) [83]. Reversal of the polarization in MFTJs changes the tunnel barrier resistance [83–86]. This effect, which has been labelled tunnelling electroresistance (TER), can have different origins [87]. In junctions with a metallic top electrode (e.g. Co, Fe, etc), TER is often explained by an incomplete screening of the polarization charges at the barrier/electrode interfaces, which for inherently different electrode materials leads to an asymmetric deformation of the barrier potential profile [88, 89]. In this case, reversal of the barrier polarization produces distinctive average barrier heights and consequently two different tunnel barrier resistances. This scenario is supported by an exponential increase in the TER effect with tunnel barrier thickness [83]. The TER effect of MFTJs can be considerably larger than the TMR of conventional MTJs.
The maximum TMR effect at room temperature is about 600% for MgO-based MTJs with CoFeB electrodes [90], which correspond to an OFF/ON ratio of 7. However, for MFTJs with a La_{0.67}Sr_{0.33}MnO_3 bottom electrode, a BTO tunnel barrier and a Co top electrode, OFF/ON ratios as high as 100 have been obtained at room temperature (Figure 12) [84]. Moreover, ferroelectric switching between two resistance states only requires a current density of about $1 \times 10^4$ A cm$^{-2}$, which is considerably smaller than the critical current density for spin-transfer torque writing in MTJs ($> 1 \times 10^6$ A cm$^{-2}$). The large, stable and reproducible TER effect underpins the potential of FTJs for data storage applications.

The TER effect is not limited to MFTJs because it does not rely on the electrodes being magnetic. Large electrical responses have also been obtained for non-magnetic top contacts [91–93]. More generally, such structures are often referred to as ferroelectric tunnel junctions (FTJs). In addition to the TER effect, however, MFTJs also exhibit a TMR response. The magnitude and even sign of the TMR effect can change upon polarization reversal in the tunnel barrier [94–96]. As an example, Figure 13 shows experimental data of a Co/PZT(3.2 nm)/LSMO junction [94]. In this experiment, switching of the polarization from pointing towards the Co to pointing towards the LSMO electrode by a $+3$ V bias voltage pulse changes the TMR response from $-7\%$ to $+5\%$ at 10 K. An opposite effect is measured when a bias pulse of $-3$ V is applied. This modification of the TMR effect is attributed to either an anti-aligned induced magnetic moment on the Ti ions at the Co interface or a spin-dependent screening effect in the LSMO interfacial layers. Support for the first scenario has been obtained by x-ray resonant magnetic scattering measurements [95] and first-principles calculations based on density-functional theory [97].

In addition to LSMO/ferroelectric barrier/metalllic electrode junctions, large TER effects have also been obtained in all-oxide MFTJs. Recently, Yin et al reported on a TER response of 5000% at 40 K in a PLD-grown 50 nm LSMO/3 nm BTO/0.4–2 nm La_{0.5}Ca_{0.5}MnO_3 (LCMO)/30 nm LSMO junction [85]. The origin of this effect is attributed to an electric-field-induced metal–insulator transition in the LCMO layer, which is driven by charge modulation. As the junction resistance depends exponentially on the barrier width, large
effects are readily obtained when only a few atomic layers of the LC1MO are affected by polarization reversal. The ability to induce a phase transition in the interfacial layers of thin-film manganites with appropriate doping concentration is supported by DFT calculations and experiments. Theoretical work by Tsymbal and co-workers indicates that the magnetic structure of the interfacial layers of La$_{0.5}$Sr$_{0.5}$MnO$_3$ changes from ferromagnetic to antiferromagnetic when the polarization in a neighbouring BTO film is rotated away from the LSMO/BTO interface [98]. A similar effect is calculated for La$_{0.5}$Ca$_{0.5}$MnO$_3$ [85]. According to the phase diagram of LSMO and LCMO, the ferromagnetic-to-antiferromagnetic transition is closely associated with a metal–insulator transition (figure 3).

Additional experimental evidence for strong electric-field effects in LSMO can also be found in the literature. For example, Hong et al demonstrated that the temperature of magnetic phase transitions and the MR response change upon polarization reversal in LSMO/PZT field-effect structures [99]. Magneto-optical Kerr effect measurements on 250 nm PZT/4 nm LSMO bilayers confirm this observation [100]. In the latter study, it is also shown that the magnetization of LSMO changes when the polarization of an adjacent PZT film is reversed between two out-of-plane states. The origin of this effect was studied in detail by Vaz et al using x-ray absorption near edge spectroscopy (XANES) [101]. In their experiments, large shifts in the absorption edge of Mn were observed, indicating a change of Mn valency due to charge carrier modulation in LSMO. Holes are depleted from the LSMO interface region when the polarization of the PZT layer points towards the LSMO film, whereas hole accumulation occurs when the polarization points in the opposite direction. These electrostatic modifications are analogous to chemical doping of LSMO. Polarization reversal can, therefore, induce large magnetic and electrical transport effects when the LSMO doping concentration is positioned near one of the phase transitions. For example, recent experiments by Lu et al indicate that electric-field control over the ferromagnetic–paramagnetic phase transition is obtained for PLD-grown La$_{0.6}$Sr$_{0.3}$MnO$_3$ films at room temperature [102].

The recent progress on electric-field-controlled effects in LSMO-based MFTJs holds a great promise for practical device applications, especially since significant and reproducible effects can be obtained at room temperature.

4.3. Organic spin valves (OSVs)

LSMO films grown by PLD are also frequently used as a spin injector in organic spintronics, an emerging research field that combines spintronics and molecular/organic electronics. In many of these studies, the LSMO layer contacts an OS, which acts as a spin transporting medium. The use of OSs in spintronics is motivated by their long spin relaxation time compared with inorganic materials, which is attributed to weak spin–orbit and hyperfine interactions in light-element compounds. Control over the electronic properties via chemical engineering, low production costs and ease of large-scale fabrication are often used as additional motivation. Several review papers have been published on organic spintronics [103–106]. Here, we only focus on the frequent use of PLD and LSMO in OSVs and MTJ devices.

The choice of LSMO in organic spintronics is mainly based on its stability in contact with OS molecules and its high degree of spin polarization. In addition, the work function (≈4.9 eV) and low carrier density of LSMO are particularly suitable for efficient spin injection into many OSs and polymers. In the first report on OSVs, Dediu et al demonstrated a MR effect of 30% at 300 K in a planar geometry with two LSMO electrodes and a 140 nm wide oligomer sexithiainyl (T6) transport channel [107]. A significantly clearer spin-valve response and MR ratio of 40% at 11 K were subsequently obtained in the first vertical spin valve with a LSMO/140 nm Alq3/Co structure [108]. However, the MR effect, which was attributed to spin-conserved hopping transport in the OS spacer layer, decayed sharply with increasing temperature. In 2006, room-temperature operation of vertical OSVs was reported for OS polymer regio-regular poly(3-hexyl thiophene) (RRP3HT) and poly(3-octylithiophene) (P3OT) based devices with a LSMO/RRP3HT/Co [109] and LSMO/P3OT/LSMO [110] structure. In the RRP3HT-based spin valves, the GMR was 80% at 5 K and the effect diminished to 1.5% at room temperature.

Many studies have been devoted to the physical origin of the strong temperature dependence of MR in OSVs [42,109–116]. In one of our efforts, we systematically investigated the influence of the LSMO electrode using PLD
on three different substrates (STO, NGO and MgO) [42]. Not surprisingly, the largest GMR values are obtained for epitaxial LSMO films on STO. However, despite the lower GMR for polycrystalline LSMO on MgO, the temperature variation of the MR effect is very similar on all substrates (left panel of figure 15). This finding suggests that the decrease in GMR signal in OSVs at elevated temperatures could be due to deteriorated spin transport in the OS spacer layer. In a later study [115], we particularly focused on polymer RRP3HT-based spin valves with LSMO and Co electrodes. Measurements on these structures indicate that despite nearly constant LSMO spin polarization in the 5–50 K temperature range, the MR response is already reduced by half (right panel of figure 15). These experimental results suggest that spin-conserved transport through the OS is obtained in the variable-range hopping (VRH) regime (at low temperatures), but that thermally activated polaron hopping destroys the spin information of the carriers at elevated temperatures. Other experiments on the detailed nature of spin scattering mechanisms in OS materials confirm this picture [113, 114, 116].

**LSMO–OS interfaces.** In addition to the LSMO electrode and the OS transport channel, properties of the LSMO–OS interface are also crucial for the GMR response of OSVs. Several experiments have focused on the electronic and spin injection properties of such interfaces. Engineering of the interface between LSMO and an OS polymer was, for example, investigated using XPS [109]. For a LSMO/RRP3HT interface, a chemical reaction between LSMO and RRP3HT was identified by studying the core-level spectra of the sulfur 2p peaks, a constituent atom of RRP3HT [109]. Once RRP3HT is coated on LSMO, the pristine LSMO surface disappeared. Cleaning with acetone and alcohol was unable to reduce the sulfur bonding and restore the pristine state of LSMO. The introduction of monolayers of two different organic insulators in the tunnelling limit, however, did partially or completely destroy the chemical bonding between RRP3HT and LSMO and this resulted in negligible spin injection. Different devices were studied with varying degrees of chemical bonding between LSMO and RRP3HT and from this it was concluded that spin injection from the ferromagnetic half-metal into the OS decreases systematically when the chemical bond is weakened. Similar chemical reactions between LSMO and organic molecules were also reported in [117]. Later a photoelectron spectroscopy (PES) study of the interface in LSMO/Alq3/Co SVs by Zhan et al [118] revealed that the introduction of OS small molecule Alq3 on LSMO creates a strong interface dipole of 0.9 eV that shifts the energy levels of Alq3 with respect to the vacuum level. Due to this energy level shift, electron injection into Alq3 becomes more favourable than hole injection. An unperturbed band diagram favours the injection of holes over the injection of electrons in Alq3. The dipole moment of the Alq3 molecule itself was suggested to be the origin of the interface dipole. They also suggested this to be the origin of the inverse sign of MR in such devices, which is still a debatable issue.

Interfacial dipole formation at the LSMO/RRP3HT interface is also confirmed by recent magneto-transport experiment [119] and by fitting the transport data with the Cheung and Cheung model [120]. This interfacial dipole modifies the barrier height for the injection of spin-polarized carriers from LSMO to the OS layer. For different crystalline qualities of the LSMO film starting from epitaxial on STO to textured on MgO, and finally to completely polycrystalline LSMO on quartz, the application and removal of RRP3HT introduces different GB-like defects in the vicinity of the LSMO surface. The introduction of more GB-like defects leads to a higher resistance and larger LFMR in epitaxial films. However, for the LSMO films on MgO and quartz, with already deteriorated crystalline and transport properties, no significant changes in MR response was found due to the addition or removal of RRP3HT layers. This result signifies that epitaxial thin films of LSMO, considered best for spin injection in polymeric spin valves, undergo degradation at the interface with OSs, extending into bulk regions, by the introduction of GB-like defects and carrier localization centres. To achieve more efficient spin injection, different interface engineering between LSMO and OS should be tested. For more details on organic–ferromagnetic interfaces including the newly coined ‘spinterface’ science, we refer to review papers on this topic [121, 122].

In addition to their usage in OSVs, OS materials have also been explored as a tunnel barrier in MTJ structures [123–125]. In many experiments, LSMO is used as the bottom electrode. While the TMR of organic MTJs can be significant at low temperatures (up to 300% at 2 K in [125]) in nano-junctions, the effect decreases sharply with temperature. Similarly to
OSVs, the deterioration of TMR at elevated temperatures is attributed to a decrease in interface magnetization in LSMO in combination with enhanced spin scattering during tunnelling transport through the OS barrier. Moreover, the TMR of organic MTJs decreases more rapidly with bias voltage than the TMR of inorganic structures. Because of this it is thought that not only magnons, which are known to play a key role in conventional MTJs, but also phonons influence the transport properties of organic junctions.

5. Conclusions and future research

Ferromagnetic half-metallic LSMO thin films have been utilized in experimental studies on spintronics for nearly two decades. During this period, several milestones have been achieved. First, the growth of LSMO thin films and its dependence on PLD growth parameters are now well understood. Second, their integration into spintronics structures has contributed to a better understanding of spin-polarized transport effects, particularly at low temperatures. In the future, LSMO will remain an important material for investigations on fundamental magnetic and electronic transport phenomena. Moreover, its instrumental use in multiferroic tunnel junctions opens up promising possibilities for commercial applications in future nanoelectronics devices. Without the development of PLD 25 years ago, the tremendous advances in complex magnetic oxides and their contribution to the spintronics research field would not have been possible. The engineering of new material properties on the atomic scale is more relevant than ever and, hence, PLD of complex interface is anticipated to unveil more interesting new physics in the future.

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