Influence of the morphology on the magneto-transport properties of laser-ablated ultrathin La$_{0.7}$Ba$_{0.3}$MnO$_3$ films

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We investigate the thickness dependent properties of manganite films characterized by colloossal negative magnetoresistance. Ultrathin, wedge-type films (0–120 Å) of La$_{0.7}$Ba$_{0.3}$MnO$_3$ were deposited by laser ablation onto SrTiO$_3$ and LaAlO$_3$ substrates. The films were patterned into strips of different thickness and magneto-transport measurements were performed at temperatures between 5 and 290 K and in magnetic fields up to 5 T. Atomic force- and transmission electron microscopy were done to correlate the microstructure with the transport data. The resistivity of the films increases slightly with decreasing thickness due to substrate-induced compressive strain. Below 50 Å, the resistivity rises abruptly indicating a crossover to discontinuous and finally island-like film growth as confirmed by the microstructural techniques. At thicknesses slightly above the threshold for percolative conduction (∼30 Å), an enhanced low-field magnetoresistance was observed as a signature of spin-dependent tunneling.

I. INTRODUCTION

Colossal negative magnetoresistance (CMR) in bulk samples of Re$_{1-x}$D$_x$MnO$_3$ (Re: rare earth, D: divalent ions) was observed fifty years ago and thereafter explained in terms of the double-exchange model. Since the discovery of CMR in thin films there is a renewed interest in these materials, see, e.g., the review articles (Refs. 4 and 5), which is motivated by fundamental aspects and by possible device applications. The substitution of divalent ions like Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, or Pb$^{2+}$ into the trivial Re-site results in a Mn$^{3+}$/Mn$^{4+}$ mixed-valency state and, depending on the substitution ratio x, a variety of magnetic phases. Between x = 0.2 and x = 0.5 these compounds show a phase transition from a paramagnetic semiconductor above the Curie temperature $T_C$ to a ferromagnetic–quasimetallic low-temperature state. Accordingly, there is a pronounced peak in the resistivity at the peak temperature $T_P = T_C$. External magnetic fields actuate this phase transition and result in the colloossal negative magnetoresistance effect, which is most pronounced in the vicinity of $T_C$. The compounds with the highest $T_C$ values and the strongest CMR amplitude are found for the doping level x ∼0.3, but the magnetic fields required for a substantial resistive drop are nevertheless as high as several Tesla.

Interesting for technological applications are, therefore, materials with pronounced low-field magnetoresistance (LFMR) as reported for manganite samples in polycrystalline form. LFMR can be interpreted in terms of spin-dependent tunneling across the boundaries between ferromagnetic grains. Mathur et al. verified the tunneling origin of LFMR by separating the contribution of a grain boundary from the total resistivity of a Wheatstone-type thin-film device. Ziese and coworkers designed step-edge arrays and observed LFMR as well, with signatures typical for spin polarized tunneling. Finally, LFMR was even observed in polycrystalline films.

To fabricate thin films with an intrinsic granularity, we will investigate the possibility of preparing manganite films in the Volmer–Weber growth mode. A suitable mismatch between the lattice parameters of the substrate and the film results, in the initial stage of film growth, in the formation of cluster-like aggregations rather than in a homogeneous layer. An enhanced LFMR should then be observed when the film thickness is such that these clusters form a percolating system on the substrate. In this ultrathin regime, it is most likely that compressive or tensile stress exerted by the substrate will affect the physical properties of the manganite layer. The key factor is the strain-induced change of the orbital overlap between the Mn$^{3+}$/Mn$^{4+}$ ions and the O$^{2-}$ ions, which controls the charge-transfer probability together with the competing ferro- and antiferromagnetic exchange interactions. Established methods for a systematic strain variation are (i) the deposition of films with a fixed thickness on different substrate materials and (ii) the fabrication of films with different thicknesses on a specific substrate material. In thicker films (thickness $t > 200$ Å) the strain is released by the formation of dislocations, while the stress...
in thinner films remains distributed homogeneously. Much less (see Ref. 22) is known about ultrathin layers (t<100 Å) where we expect a Volmer–Weber-type growth.

In this article, we study the thickness dependence of morphology and transport properties of laser- ablated, ultrathin films (0–120 Å) of La_{0.7}Ba_{0.3}MnO_3 (LBMO). This material has, in bulk form, a rather high Curie temperature (T_C ~320 K) and the pseudocubic lattice constant is 3.92 Å. To fulfill the preconditions for Volmer–Weber growth, we chose slightly “compressive” substrate materials, namely (1 0 0)-oriented SrTiO_3 (a = 3.905 Å) and LaAlO_3 (a = 3.82 Å). Since we are interested in a situation with percolating grains, it is less suitable to use samples with discrete thickness, because the transition from nonconnected clusters to a coherent film might happen within a narrow thickness interval. Therefore, we opted for a smooth thickness gradient on the same substrate by depositing wedge-type films—a technique, which is well established in the fabrication of metallic multilayers with giant negative magnetoresistivity. 23 A second advantage of this method is to eliminate the influence of parameters like the substrate morphology and the exact reproducibility of the deposition temperature.

II. EXPERIMENTAL

Epitaxial thin films of LBMO were made by pulsed laser deposition from dense stoichiometric targets. The wavelength of the frequency-tripled Nd–YAG laser was λ = 359 nm, the repetition rate of the 6 ns pulses was 10 Hz, and the pulse energy 250 mJ. First, we optimized the preparation parameters by depositing 1000 Å thick LBMO films (without wedge structure) onto (1 0 0)-oriented SrTiO_3 and LaAlO_3 substrates (10×10×1.2 mm^3). Epitaxial, single phased films were formed in an atmosphere of 0.26 H Pa flowing oxygen with heater-block temperatures between 800 and 850 °C. To improve the oxygenation and lower the resistivity of the samples, we performed after deposition an additional ex situ annealing for 12 h at 900 °C in air. The pseudocubic lattice constant of the postannealed films was 3.92 ± 0.02 Å, with a full width at half maximum of the rocking curves below 0.35°. The Curie temperature, as determined by a superconducting quantum interference device magnetometry, was T_C = 289 K.

The wedge-type films were prepared under the same conditions, using a manually driven shutter in front of the substrate. To induce the wedge-type thickness gradient, the shutter was opened in steps of 1.0 mm, with a duration of 6 s between the individual steps. The “thick” side of the substrate was thus exposed to the laser plume during 60 s, corresponding to a film thickness of 120 Å, while the coverage at the thin side was negligible. The thickness profile between can be considered as a smooth wedge. The morphology of the thin films was then investigated on various positions of the substrate by atomic force microscopy (AFM) in noncontact mode. The error in all thickness- and roughness measurements was below 5 Å. Scanning-probe techniques like scanning tunneling- or magnetic force microscopy are not suitable in this case, because of the low conductivity of the samples (nonconnected clusters at the thin end) and the Curie point being below room temperature. The morphology of a LBMO wedge on SrTiO_3 was thereafter studied by transmission electron microscopy (TEM). Cross section samples were prepared by standard techniques using mechanical polishing followed by ion-beam milling under grazing incidence. The high-resolution electron microscopy (HREM) images were obtained using a JEOL 4000 EX microscope operating at 400 kV with a point resolution in the order of 1.7 Å.

To obtain a well-defined geometry for transport measurements the films were patterned by optical lithography and wet chemical etching. The pattern (see Fig. 1) consists of 11 separate strip lines, each with a length of 1000 µm and a width of 200 µm, while the distance between the individual strips is 500 µm. Evaporated and annealed gold pads serve as current and voltage probes in four-point geometry. The magneto-transport measurements were performed in a He flow cryostat with a variable temperature insert at temperatures between 5 and 290 K. The direction of the magnetic field was in the substrate plane, parallel with the measuring current (pulsed current of 10 nA with alternating polarity to eliminate thermal voltages). This way, resistances could be measured up to 25 MΩ, which turned out to be essential for the thinnest stripes of the pattern. The transport measurements on all stripes were done in a four-step cycle: (i) at 290 K, in the paramagnetic regime of LBMO, the field was swept from 0 to 5 T, (ii) the sample was cooled from 290 to 10 K in a persistent field of 5 T, (iii) at 10 K, in the ferromagnetic low-temperature state, the field was reduced from 5 T to B
=0, and (iv) finally, the sample was warmed up from 10 to 290 K in zero field.

III. MORPHOLOGY

Figure 2 shows AFM images of the surface morphology of an LBMO film on a LaAlO$_3$ substrate at three different positions, being 0.7, 2.3, and 7 mm away from the thin edge of the wedge. AFM images of LBMO wedges grown on SrTiO$_3$ substrates show widely identical features as those on LaAlO$_3$. In Fig. 2(a), the substrate is very sparsely covered. There are about $n_e = 22$ clusters visible with a mean average surface $a_e = 4000$ nm$^2$. The roughness of the regions between these clusters corresponds to that of the bare substrate, pointing to the expected Volmer–Weber type growth. The possibility of Stranski–Krastanov growth, characterized by clusters on a continuous seed layer, can be excluded. The average maximum height of the clusters in Fig. 2(a) is $h = 30$ Å. The surface-covering ratio at this position is thus $(n_e \times a_e)/1 \, \mu m^2 = 8\%$. According to the percolation theory, in two dimensions the covering ratio should exceed the threshold value of 25% (for disk-shaped objects of uniform size) to obtain any percolating path. This implies that at 0.7 mm from the thin edge of the wedge, the film will behave as an insulator. In Fig. 2(b), at 2.3 mm from the thin edge, the number of clusters has increased to $n_e = 56$ while the average height and surface per cluster stay almost the same. The resulting surface coverage is 22%, still slightly below the percolation limit, which should be reached at a position around 3 mm from the thin edge. Figure 2(c) shows the AFM image at 7 mm from the thin edge of the wedge. There are no individual clusters anymore but a continuous film with an average surface roughness of 15 Å. This pronounced roughness indicates that the film still has some remnant granularity, which could not be observed in our 1000 Å thick samples.

Figure 3(a) shows a high-resolution, cross-section TEM image along the [1 0 0]-axis of the LBMO film grown on SrTiO$_3$ at 2.0 mm from the thin edge. Although the film and substrate both have the perovskite structure, the film can be distinguished by a difference in contrast, which was verified by image simulations. The substrate is not completely covered by the film, as can be seen from the left-hand part in Fig. 3(a) where the film ends. This confirms the AFM result that the films show cluster-like island growth at the thin edge. The island height here is 7 unit cells, corresponding to 28 Å, in agreement with the AFM measurements. Because of the small film thickness the lattice parameter of the film along the substrate–film interface has adapted to the lattice parameter of SrTiO$_3$ (3.91 Å ± 0.02 Å). No interface dislocations or strain relaxation have been observed within the resolution of our TEM experiment. Note also that the film is atomically flat and surface steps do not occur, except near the
edge of the island. Cross section HREM images of the same film at 2.0 mm from the tick edge show a complete coverage of the substrate by the film, see Fig. 3(b). Diffraction patterns, as well as the HREM measurements, indicate no difference between the lattice parameters of SrTiO$_3$ and the Mn perovskite. Consequently, there are no dislocations along the interface. The film thickness is 105 Å, in agreement with the estimate from the deposition time and AFM measurements on patterned strips. Twinning or other planar defects, typical features of crystals with a Pnma-type symmetry, are absent in these films.

IV. RESISTIVITY

Figure 4 shows the resistivity of two selected strips on SrTiO$_3$ measured as a function of temperature at two magnetic field values. The thicknesses of 90 Å and 32 Å were chosen as representative values, respectively, for samples with a continuous layer, and a discontinuous film with percolating clusters. Note that the indicated thicknesses at the thin side (≤50 Å) are nominal values: the height of several strips at the thick end was measured by AFM, and these results were extrapolated to the thin, discontinuous edge. The resistivity of the thicker film (32 Å) is enhanced by roughly one order of magnitude compared to the 90 Å film, but the characteristic semiconductor–quasimetals transition and the CMR effect are still present. The 90 Å strip has its resistive peak temperature $T_p = T_c$ close to 295 K. This is even slightly higher than in the 1000 Å thick reference films on SrTiO$_3$ ($T_p = 289$ K). For temperatures below 120 K, the CMR effect vanishes as expected for films with long-range ferromagnetic order. The residual resistivity for $T \to 0$ is still relatively high (1 mΩ cm), which might be due to remnant grain boundaries.

The cluster strip with 32 Å shows different features. Firstly, the peak temperature, indicating the onset of ferromagnetic correlations, is shifted by 80 to 216 K. Secondly, the resistivity is considerably enhanced (to 137 mΩ cm instead of 28 mΩ cm at $T_p$), suggesting that grain-boundary resistance starts to play an important role. Thirdly, the CMR effect in 5 T persists even in the low-temperature limit, indicating that the individual clusters are not in a coherent ferromagnetic state. Finally, there is a curling up of the resistivity below 50 K, which is a signature of tunneling across grain boundaries. The wedge-type LBMO films on LaAlO$_3$ substrates show, qualitatively, the same features.

The resistivity as a function of the stripe thickness is shown in Fig. 5. As a reference temperature, we used $T_p$ (see insert of Fig. 5), which is well-defined since the degree of magnetic disorder is comparable for all stripes, which would not be the case when comparing the resistivity data at a fixed temperature. Above 60 Å, there is no significant thickness variation of the peak resistivity, neither for LaAlO$_3$ nor for SrTiO$_3$ substrates. In the case of SrTiO$_3$, this could be expected from the TEM images, showing that there is no measurable difference in the lattice parameter of LBMO at the thick and the thin edge. The strain, if any, should be uniform in the entire region. The peak resistivities for LaAlO$_3$ are, for all thicknesses, three to four times higher than the corresponding data on SrTiO$_3$, which is caused by the stronger compressive strain exerted on the LBMO film. There are two distinct mechanisms, which can explain the strain-induced reduction of the conductivity: (i) strain can promote the growth of relatively small grains with, consequently, a large contribution of intergranular boundaries. According to the AFM studies, there is a slight increase in the number of grains in the films on LaAlO$_3$, but this is insufficient to account for a factor of 3 difference in the resistivity and (ii) a second mechanism is more plausible and involves the influence of strain on the orbital configuration of the manganite layer. The $3d-e_g$ electrons of Mn$^{3+}$ induce a Jahn–Teller distortion in the surrounding O$^2-$ octahedra, which can either be of the elongated type ($3z^2-r^2$ orbitals) or of the compressed type ($x^2-y^2$). A compressive substrate will favor the elongated deformation, with the $3z^2-r^2$ orbitals...
standing perpendicular on the substrate surface. This out-of-plane orientation decreases the charge transfer probability between the Mn ions within the substrate plane, i.e., the direction of electric transport. Additionally, the in-plane compression enhances the orbital overlap between the $3d^{-1}t_{2g}$ electrons via the $O^{2-}$ sites, and consequently the antiferromagnetic superexchange. As a result, the Curie temperature of the system should decrease upon compression. The insert of Fig. 5 shows that the $T_p$ values ($=T_C$) for films on LaAlO$_3$ are systematically 50 K lower than in the case of a SrTiO$_3$ substrate.

Below a thickness of $\approx$50 Å LBMO shows an abrupt rise of the resistivity for both substrates, together with a substantial drop of the peak temperature. According to the AFM data, the films become discontinuous in this regime and the transport is presumably dominated by two-dimensional (2D) percolation between weakly connected clusters. The magnetic properties of these clusters should deviate from bulk material because the surfaces, which break the symmetry together with magnetic interactions, become much more important. Recent magnetization studies on the surface and the bulk of manganites point also into this direction. For film thicknesses around and below 25 Å, the resistivities became too high to be measured.

It was recently pointed out by Sun et al. that the increasing resistivity upon decreasing film thickness can indicate the presence of a dead layer at the interface with the substrate. The term “dead layer” suggests that this film sheet is insulating and nonmagnetic (e.g., due to chemical interdiffusion with the substrate), but is also used for layer thicknesses where there is just no percolating path between the island-like grains. To distinguish between these two possibilities, we plotted the conductance as a function of the stripe thickness in Fig. 6. The reference temperature is 20 K, because the conductances show here a negligible temperature variation and correspond to residual values. For SrTiO$_3$, we can extrapolate the conductance of the three thickest strips, albeit with some uncertainty, through the origin (see dashed line in Fig. 6), which makes the presence of an insulating interface layer improbable. Therefore, we rather tend to the interpretation that the vanishing conductivity below 30 Å is caused by the absence of percolation between islands, which might on their own still be conducting and ferromagnetic. This explanation is supported by the morphological studies: at a nominal film thickness of 30 Å there is a surface coverage of 29%, which is slightly above the ideal 2D percolation limit of 25%. The percolation threshold for 2D objects with a random size and shape distribution can be as high as 50%. Our experimental value of 29% is thus much closer to the prediction for disks of equal size, in agreement with the AFM images shown in Fig. 2. The nonpercolating layer thickness for the LaAlO$_3$ substrate has roughly the same value as for SrTiO$_3$: the resistance diverges around 27 Å.

V. MAGNETORESISTANCE

The thickness dependence of the CMR effect in an external field of 5 T is shown in the Figs. 7(a) and 7(b) for SrTiO$_3$ and LaAlO$_3$ substrates, respectively. As representative temperatures for the CMR ratio $(\rho_0-\rho_{ST})/\rho_0)$, we chose 10 K, 290 K, and the peak temperature $T_p$ of the zero-field resistivities.

At 290 K, i.e., in the paramagnetic regime, there is a systematic decrease of the CMR ratio with decreasing film
thickness, which can be interpreted as follows. A decreasing thickness causes a drop of the ferromagnetic ordering temperature and results therefore in an enhanced spin disorder at 290 K > T_C (compare inset of Fig. 5). Consequently, external magnetic fields become less effective in inducing a parallel spin alignment, which is reflected by the paramagnetic CMR-scaling relation \( \rho(B)/\rho_0 \propto M^2(B, T) \). The magnetization \( M(B, T) \) depends on the external field \( B \) and the temperature \( T \) according to the Brillouin function \( B(B, T) = (T - T_C) \). As a result, the magnetization at the fixed conditions \( B = 5 \) T and \( T = 290 \) K will decrease as the films become thin and the CMR effect diminishes.

An interesting feature is the increase of the CMR ratio at the resistive peak temperature, which corresponds approximately to the maximum possible CMR effect for a given stripe thickness. At the thick edge of the films, we obtain a 50% CMR effect for SrTiO\(_3\) and 70% for LaAlO\(_3\), increasing at the thin side to 70% for SrTiO\(_3\) and even 85% for LaAlO\(_3\). This CMR enhancement at \( T_P \), upon decreasing thickness might emerge from the thickness dependence of \( T_P T_C \), itself. At the thin end, \( T_P \) for LaAlO\(_3\) is as low as 120 K, meaning that the semiconductor to quasimetal transition occurs under conditions where the resistivity difference between both conductor types is especially large. As a result, the CMR amplitude is unexpectedly enhanced.

The thickness dependence of the CMR ratio at 10 K is opposite to the evolution at 290 K, which can be seen for LBMO on SrTiO\(_3\) in Fig. 7(a). The CMR ratio increases from 2% for a 90 Å strip to 17% for a nominal film thickness of 32 Å, characterized by percolating clusters. The properties for LaAlO\(_3\) are comparable (25% for 32 Å, see Fig. 7(b)], with a slight decrease when entering the regime below 30 Å. \(^{30}\) The Curie temperature is, also in case of the cluster films, much higher than 10 K, meaning that the ferromagnetic spin structure within the individual clusters is fully developed. The enhanced low-temperature CMR is therefore caused by the specific morphology, which promotes a spin-dependent intergranular transport, possibly in the sense of magnetic tunneling.

To probe the possibility of spin-dependent tunneling, we measured the magnetoresistance at 5 K as shown for SrTiO\(_3\) in Fig. 8. The resistivities are normalized to their zero-field value. The change of \( \rho \) as a function of the applied field is negligible for the 90 Å strip (<2%), while the 32 Å strips has a remarkable CMR of 18% at 5 T. For LaAlO\(_3\) we found similar features. A criterion for spin-dependent tunneling in polycrystalline samples is a sharp resistive drop in low magnetic fields, which can eventually be followed by a weaker resistance decrease in high fields.\(^{6}\) The curves in Fig. 8 do qualitatively show these properties. This can be seen from the two distinct field regions of the derivatives \( d(\rho/\rho_0)/dB \) shown in the inset: the derivatives are strongly enhanced below 250 mT, and become flat above this field range. Interestingly enough, there is also an enhanced, but less pronounced low-field slope present in the data for thicker strips (40 to 90 Å), which indicates that also apparently continuous layers can show some remnant granularity.

FIG. 8. Normalized resistivity vs magnetic field for selected LBMO strips on SrTiO\(_3\) at \( T = 5 \) K are shown. The 32 Å strip exhibits a 14% resistivity increase at 5 T. The field derivative of the normalized resistivities is given in the inset. Especially the thinnest strip shows signatures of spin-dependent tunneling, namely a strongly enhanced slope in the low-field limit with \( B < 250 \) mT.

VI. CONCLUSIONS AND SUMMARY

LBMO films with a wedge-type thickness gradient were grown by pulsed laser deposition on SrTiO\(_3\) and on LaAlO\(_3\) substrates. There are three distinct thickness regimes characterized by different electronic and morphological properties: Above 60 Å, the films are continuous and uniformly strained. Resistivity, magnetoresistivity, and the Curie temperature show a negligible thickness dependence and can be, as far as films on SrTiO\(_3\) are concerned, closely compared to the properties of bulk material. LaAlO\(_3\) exerts a stronger compressive strain the films, which lowers the Curie temperature together with the conductivity. Both features can be explained in terms of a strain-induced orbital configuration, with the 3d-\( \epsilon_s \) electron orbitals standing preferably perpendicular to the film plane. In the thickness range from 60 down to 30 Å, we observed a rapid increase and finally a divergence of the film resistivity, which is caused by a breaking up of the layers into granular, percolating islands. The cluster-type structure hinders the evolution of long-range ferromagnetic order and shifts the para- to ferromagnetic transition to lower temperatures. At a film thickness above the percolation limit, we observed an enhanced negative magnetoresistance at low temperatures and in low fields (<250 mT), which is typical for spin-dependent tunneling between individual grains. Below the percolation limit at about 27 Å, the films consist of nonconnected clusters, suggesting a growth mode of the Volmer-Weber type.

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30. The 28 Å strip in LaAlO3 behaves at 10 K as a semiconductor with $\rho(T_F) > \rho(T)$ This is in contrast to all other strips, being quasimetallic at lowest temperatures.