Transport properties of microstructured ultrathin films of La0.67Ca0.33MnO3 on SrTiO3

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Transport properties of microstructured ultrathin films of $La_{0.67}Ca_{0.33}MnO_3$ on $SrTiO_3$

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We have investigated the electrical transport properties of 8 nm thick $La_{0.67}Ca_{0.33}MnO_3$ films, sputter-deposited on $SrTiO_3$ (STO), and etched into 5 μm-wide bridges by Ar-ion etching. We find that even slight overetching of the film leads to conductance of the STO substrate, and asymmetric and non-linear current-voltage (I-V) characteristics. However, a brief oxygen plasma etch allows full recovery of the insulating character of the substrate. The I-V characteristics of the bridges are then fully linear over a large range of current densities. We find colossal magnetoresistance properties typical for strained LCMO on STO but no signature of non-linear effects (so-called electroresistance) connected to electronic inhomogeneites. In the metallic state below 150 K, the highest current densities lead to heating effects and non-linear I-V characteristics.

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Doped manganese oxides such as $La_{1-x}Ca_xMnO_3$ are of interest since, in a certain range of doping, a combined insulator-to-metal and paramagnetic-to-ferromagnetic transition can take place. One consequence is the well-known Colossal Magnetoresistance effect, but another is the fundamentally interesting phenomenon of phase separation. The susceptibility of the phase transition to chemical and crystallographic disorder (doping disorder, oxygen non-stoichiometry, defects from strain relaxation, twinning, grain boundaries) can lead to an inhomogeneous state in which the insulating and metallic phases coexist on a variety of length scales. In such systems, the percolative nature of the conductance may lead to strongly non-linear behavior and a large sensitivity to electric fields, which can be useful for a variety of applications. Lately, therefore, there has been renewed focus on conductance issues, leading to various different observations. Non-linearities, presented as a strongly decreasing resistance as function of increasing current density, were reportedly measured on microbridges made from films of $La_{0.7}Ca_{0.3}MnO_3$ and $La_{0.85}Ba_{0.15}MnO_3$ grown on STO [1]. Similar observations were reported on samples made with $La_{0.7}Ca_{0.3}MnO_3$ [2]. In both cases it was suggested that these so-called electroresistance (ER) effects are due to phase separation. In other experiments, microbridges were subjected to high currents ("current processing"), and non-linear as well as asymmetric current-voltage (I-V) characteristics were subsequently found in the two-point resistance [3, 4]. This was tentatively ascribed to the formation of junction-like structures in the films, and therefore intrinsic, although modification of the interface between the metal electrodes and the oxide film by the current was not fully ruled out. The interface is a known complication in 2-point geometries; non-linear and asymmetric I-V characteristics were demonstrated in rectifying $Ti/Pr_{0.7}Ca_{0.3}MnO_3$ contacts [5], in a *p*-*n* heterostructure involving $La_{0.7}Ca_{0.3}MnO_3$ and Nb-doped $SrTiO_3$ (STO) [6], and in Ag-$La_{0.7}Ca_{0.3}MnO_3$ heterostructures [7]. However, 4-point measurements on $La_{0.8}Ca_{0.2}MnO_3$ microbridges also showed current-induced ER [8, 9], and it was concluded that high currents can change the balance in the coexistence of the different phases. All of the above microbridges are still relatively large, with typical film thicknesses of 100 nm and bridge widths around 50 μm. Phase separation phenomena may be found down to very small length scales, in particular when strain and strain relaxation also play a role [10, 11]. The question then arises whether similar ER effects can be seen in smaller bridges and thinner films. Here we note that special care has to be taken in the structuring. The commonly used Ar^+-etching technique easily damages the STO substrate, which results in a conducting surface layer after etching [12]. Current leakage through this layer interferes with the transport measurements and intrinsic current effects will be obscured. This problem can be overcome by a brief oxygen plasma etch, as will be shown below.

Epitaxial films of $La_{0.67}Ca_{0.33}MnO_3$ with a typical thickness of 8 nm were grown on (001)STO substrates by DC sputtering in an oxygen pressure of 300 Pa, at a growth temperature of 840°C. The substrate surface was treated to have single termination of TiO_2, and had a misorientation of 1° towards [010] in order to improve the smoothness of the film. A resist mask was patterned by e-beam lithography to yield a structure for 4-point measurements, with a bridge width of 5 μm, a distance between the voltage contacts of typically 16 μm and the orientation of the bridge perpendicular with respect to the step edges of the substrate. The film was etched with Ar-ions (beam current: 10 mA, beam voltage: 350 V) during 40 s; with a calibrated etch rate 0.31 nm/s, this means overetching of 14 s, in order to be certain to remove all of the film. Temperature and magnetic field regulation were done in a Physical Property Measurement System (PPMS: Quantum Design) but external current sources and nanovoltmeters were used to perform most of the transport measurements.

I-V characteristics were measured on the microbridges in the temperature range of 10 K - 300 K using currents

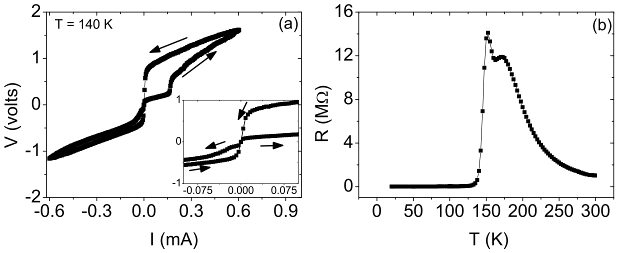

FIG. 1: (a) I-V curve at T = 140 K of an LCMO bridge on STO after 14 sec overetching; insert : behavior near zero current); (b) Resistance measured as averaged voltage (see text) versus T of the same sample.

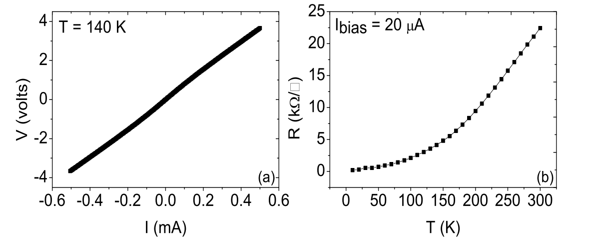

FIG. 2: (a) I-V curve of 30 sec Ar-etched STO (1.5 x 2.6 mm^2) at T = 140 K; (b) R-T plot of the same sample obtained from the I-V curves at 20 μA.

up to 0.6 mA, which corresponds to a current density $J = 1.5{\times}10^{10}$ A/m^2. A typical one, taken at 140 K, is shown in Fig.1a. It shows nonlinearity and a large asymmetry between opposite current directions, as well as hysteresis at high J. Similar curves could be observed at all temperatures. Still, by simply averaging voltages at small positive and negative currents (0.1 μA; this was performed with the PPMS electronics) the 'resistance' R (Fig.1b) shows a sharp phase transition at 150 K, as expected for films under tensile strain [13]. Apparently, the measurements at least partly probe the bridge structure, but since this is a 4-point measurement, the asymmetry indicates that not all current is flowing between the voltage contacts. It is known that Ar etching of STO causes the formation of a conducting surface layer by the removal of oxygen [12]. To conclusively show this in our system, we etched a $w = 1.5$ mm wide STO substrate for 30 sec. After etching, 4 Au/MoGe contacts [14] where sputtered on top ($\ell = 2.6$ mm between the voltage contacts). The I-V curves (Fig.2) are symmetric down to 150 K, although below this temperature they become slightly nonlinear. Fig.2 also shows the T-dependent sheet resistance $R_\Box = Rw/\ell$ obtained at low bias. The dependence is metallic, $R_\Box$ is very close to the number reported in ref. [12], but also important to note is that the absolute value of R is in the range of (only) 1 kΩ - 10 kΩ, which makes it substantially smaller than the expected peak value for R in our microbridge, or even for R in significantly wider and thicker bridges.

In order to restore the insulating properties of the substrate, post-annealing in an oxygen environment would probably be possible, but this is often unwanted as a process step; in our case, it might lead to strain relaxation and additional defects in the film. Instead, after the Ar-etch we subjected structures with the resist still in place to an O_2 plasma for typically 1 - 2 min. and found that the substrate had become insulating again while resist was still present. Generally, the procedure appears to work for small amount of etching of the STO. Substrates which were Ar-etched for more than 1 min. did not show recovery anymore, even after 4 min. of plasma treatment (by which time the resist layer had been removed). We surmise that oxygen loss can be recovered by the plasma, but that more structural damage to the STO (amorphisation) renders this impossible.

In Fig. 3 we show an I-V curve and the R(T) plot for a microbridge which was overetched by 4 sec and then plasma-treated. The result clearly shows that when the STO substrate is restored to its insulating state, the microstructured LCMO thin film has linear and symmetric I-V characteristics in four point measurements. No electroresistance is observed in our LCMO bridges. Note that

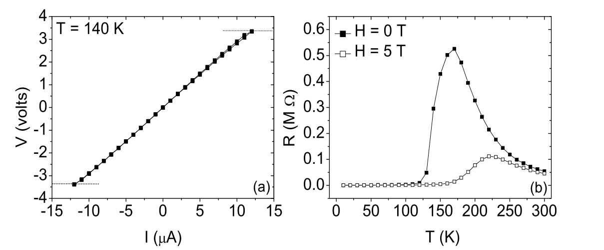

FIG. 3: (a) I-V curve at T = 140 K of an LCMO bridge on STO after 4 sec overetching and O_2-plasma treatment. The thin lines indicate the voltage limit for the measurement; (b) R-T plot at magnetic field B = 0 T and 5 T of the same sample.

the current densities we used, between 2.5x10^7 A/m^2 and 1.5x10^{10} A/m^2, lie within the range for J where large resistance variations were reported in refs. [1, 2]. In those cases no details are given about I-V characteristics or the effects of microstructuring, but the samples are different from ours, since they are typically 100 nm thick. A possible explanation for the quite strong discrepancies is that our films are very homogeneous even on submicrometer scales, in particular since strain relaxation has not yet set in. It seems probable that the grain structure and the disorder in the films determine possible ER effects to a large degree, as was surmised in ref [2].

To observe possible effects of the contacts we also measured the treated sample in a two-probe configuration, with current injected through the voltage pads. The results are shown in Fig. 4 where we compare the I-V curves

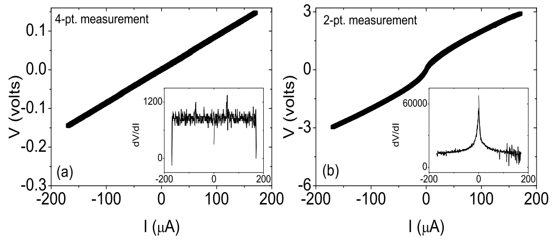

FIG. 4: I-V curves of an LCMO bridge on STO at T = 10 K (a) in 4-point configuration; (b) in 2-point configuration. Insets show derivatives dV/dI.

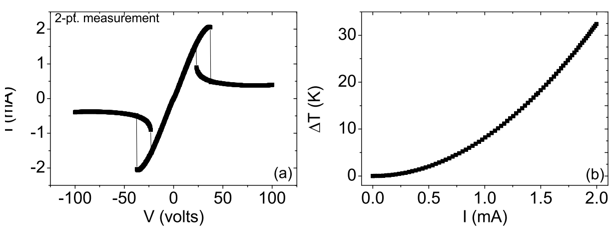

FIG. 5: a)I-V curve of an LCMO bridge on STO at T = 50 K measured in a 2-point configuration. b) Calculation of the expected Joule heating (see text) represented as temperature increase ΔT versus applied current I.

for two and four point measurements taken at 10 K. The 4-point measurement shows a linear and symmetric IV curve as expected. The 2-point resistance is significantly larger (around a factor of 5 after correction for the extra lead resistance in the contact pads). This can be attributed to a large contact resistance. Another feature is the nonlinearity of the I-V curve, with the corresponding peak in the derivative dV/dI (see inset) clearly visible and most probably caused by the presence of a barrier at the contact-film interface.

In the 2-point measurements in the metallic state we also found nonlinear effects in the I-V characteristics which we ascribe to Joule heating. A measurement at 50 K is shown in Fig.5a where the voltage-driven system suddenly switches to a lower current (higher resistance). It is not straightforward to make an estimate of the effect. The measured resistance is dominated by the contacts, but the area of the contacts is much larger than the bridge so that it is not a priori clear in which part of the structure the heating occurs. If we still assume it is the bridge, we can estimate the temperature increase ΔT from a current I using the following equation taken from [15], $\Delta T(T,I) = (2I^2\rho(T+\Delta T))/(S\kappa_{sub}(T+\Delta T)$, with ρ(T) the specific resistance of the bridge at temperature T, S its cross-section, and κ the thermal conductance of the substrate. Taking ρ(T) in the metallic state independent of temperature and use the value $\rho = 260\ \mu\Omega cm$ found in the 4-point measurement, then with $\kappa = 16$ $WK^{-1}m^{-1}$ [16], we find Δ(T) $\approx$ 30 K at 2 mA (Fig.5b). The model is quite crude, but the result at least indicates that heating effects cannot be negelected in our bridges. The mechanism leading to the switching behavior is not yet understood, however, and needs further investigation.

In summary we conclude that the observed peculiarities in the I-V characteristics of our films are caused by the Ar-etching and are not an intrinsic feature. We can restore the insulating STO surface layer by an O_2 plasma treatment and then find no electroresistance effects in our thin and homogeneous films. We further demonstrated that contact resistance and Joule heating can introduce non-linear effects which are not intrinsic to the material under study.

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