Very large magnetoresistance and coherent switching in half-metallic manganite tunnel junctions

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We have fabricated spin polarized tunneling devices based upon half-metallic manganites ($La_{0.7}Ca_{0.3}MnO_3$) incorporating $NdGaO_3$ as a barrier material. These devices show high tunnel magnetoresistance (TMR) values above 77 K and coherent switching with a qualitatively different dependence of resistance on magnetic field to previous devices. The electron polarization deduced from measurements at 77 K is higher than the directly measured value at 4.2 K: we suggest an active tunneling mechanism based on percolative phase separation to account for the general TMR temperature dependence in these materials and the high spin polarization in particular.

Spin polarized tunneling (SPT) between ferromagnets, which exploits the energy splitting in the density of states of up- and down-spin electrons, has received considerable recent attention both because of the important underlying physics and the potential applications in magnetoelectronics.[1] The tunnel magnetoresistance (TMR) can be given by

$$\mathrm{TMR}=\Delta R/R_{AP}=(R_{AP}-R_P)/R_{AP},$$

where R_{AP} and R_P represent the junction resistances when the two ferromagnets have antiparallel and parallel magnetizations, respectively. This TMR definition, by which we define all the TMR results, sets an ultimate upper limit as 100%. The other standard definition of TMR in the literature (usually applied to tunnel junctions with metallic electrodes) is $\Delta R/R_P=(R_{AP}-R_P)/R_P$; in this case the value can tend to infinity. In ''half-metallic'' materials such as the mixed valance manganites ($La_{1-x}Ae_xMnO_3$, where Ae is an alkaline earth) the relatively narrow spin up and down conduction bands are completely separated leading to 100% polarization at low temperatures[2,3] and thus these materials have been recognized for several years as being good candidates for the study of spin polarized tunneling.[4–7] However, TMR devices incorporating such materials have yielded reproducible tunnel magnetoresistance (TMR) values only at the lowest temperatures, and even these values are well below those predicted on the basis of the independently measured polarization ($>75\%$).[8] The magnetic properties of these materials are highly sensitive to local crystal properties and the extrinsic strain fields induced by the lattice mismatch with the substrates or tunnel barriers can be sufficient to severely degrade the ferromagnetic order in the surface layers which are critical for tunneling.[9] Here we describe devices incorporating a barrier material which have yielded coherent switchings and very high TMR values above 77 K. The results provide direct evidence for high spin polarization of half-metallic materials at high temperatures and demonstrated the feasibility of maximizing TMR.

In this study we selected $NdGaO_3$ for the substrate and tunnel barrier because of its low lattice mismatch ($<0.08\%$) with $La_{0.7}Ca_{0.3}MnO_3$(LCMO) electrodes. LCMO/$NdGaO_3$LCMO trilayers were grown *in situ* by pulsed laser deposition[9] (KrF laser, 248 nm) using stoichiometric targets at 600–800 °C in a flowing oxygen atmosphere of 15 Pa with layer thickness of 80 nm (bottom)/ 2.5–3 nm/60 nm (top). Heteroepitaxial trilayer growth on $NdGaO_3$ substrates exhibits a typical layer-by-layer growth mode indicating the high quality of the heteroepitaxial structure. As shown in Fig. 1, the surface of the trilayer consists of atomically flat terraces with one unit-cell height ($\sim$0.4 nm) which is essentially the same as the original substrate with miscut angle of $<0.6°$. Devices were patterned from LCMO / $NdGaO_3$ /LCMO trilayers using optical lithography and Ar ion milling to produce mesas with a range of areas between 36 and 600 μm^2; the structure of the complete device is shown schematically in Fig. 2(a). Four terminal measurements of the tunneling resistance were performed as a function of magnetic field (applied in the substrate plane) and temperature.[10] The resistance of the common base electrode could be independently measured; generally this showed a Curie temperature (T_C) of 265 K which is similar

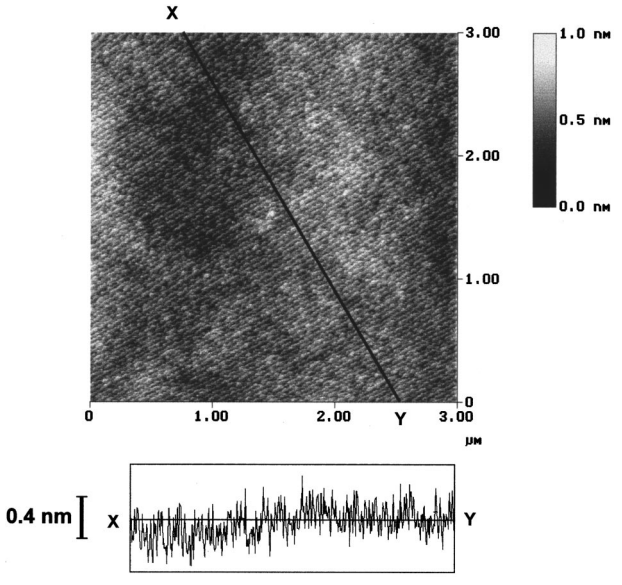

FIG. 1. The surface AFM image of the LCMO/$NdGaO_3$ /LCMO trilayer (3×3 μm^2). The cross-sectional line profile shows that each step height corresponds to one unit-cell thickness of pseudocubic perovskites in a given heterostructure.

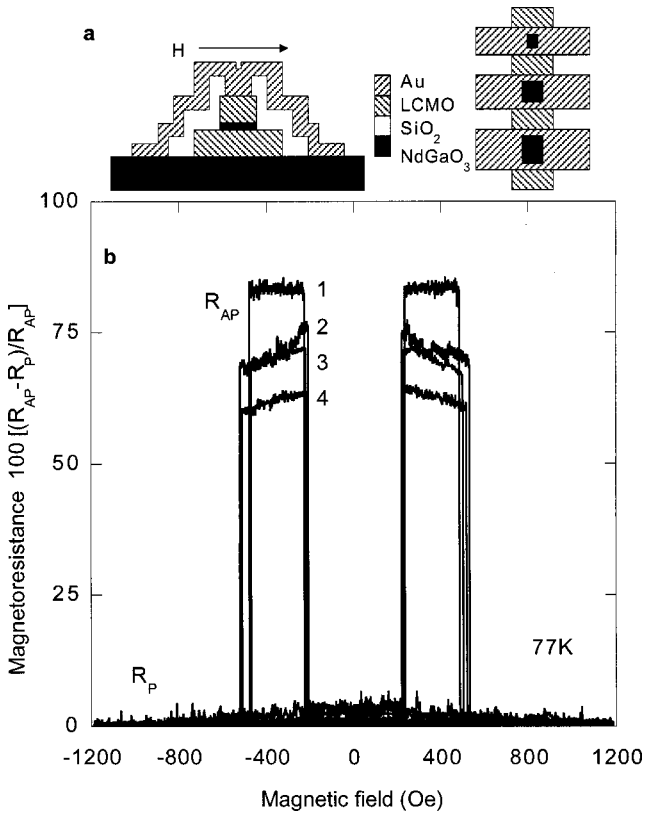

FIG. 2. (a) Schematic diagrams of the cross-section (left) of a typical device and (right) plan view of several devices on a common base electrode. (b) Junction resistance versus applied magnetic field. The tunnel magnetoresistance, defined as $(R_{AP}-R_P)/R_{AP}$, at 77 K for four $La_{0.7}Ca_{0.3}MnO_3/NdGaO_3/La_{0.7}Ca_{0.3}MnO_3$ junctions, showing a maximum change of a factor of 7.3 between parallel (R_P) and antiparallel resistances (R_{AP}) and the coherently sharp switching at two well-defined fields. Junction areas (1) $6\times6\ \mu m^2$, (2) $8\times8\ \mu m^2$, (3) $8\times16\ \mu m^2$, (4) $20\times30\ \mu m^2$.

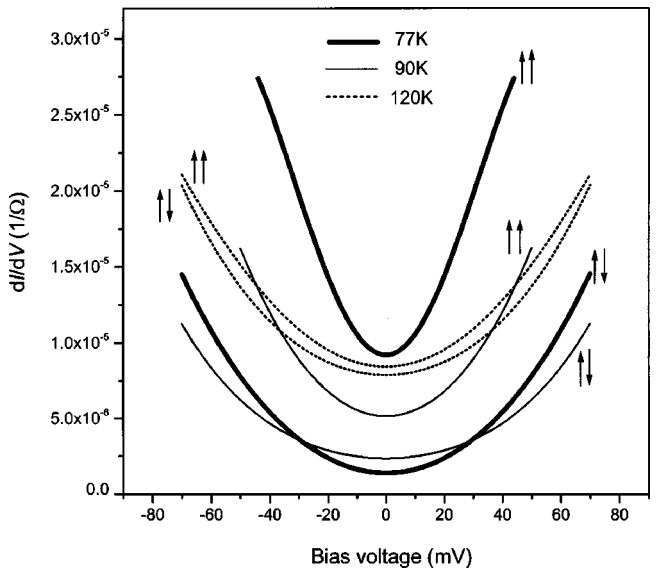

FIG. 3. The dynamic conductance dI/dV of junction (1) from Fig. 1(b) versus bias voltage for parallel (1000 Oe) and antiparallel (350 Oe) spin states at different temperatures. All curves can be accurately fitted by a function of the form $dI/dV=A+BV^2$, where A and B are constants which depend on the temperature and magnetization alignment.

to that of unpatterned epitaxial single films. The base electrode sheet resistance at low temperatures was several orders of magnitude lower than the junction resistance which ensures a uniform current distribution across the barrier and thus any possible geometrical MR enhancement can be eliminated.[11]

All the devices measured showed very large magnetoresistance at low temperatures, with extremely sharp switching between the high and low resistance states which we assume to correspond to antiparallel and parallel alignment of the moments of the two LCMO electrodes. Figure 2(b) shows the resistance at 77 K versus magnetic field of a number of junctions from the same chip. Two striking characteristics are evident: first the measured TMR {defined as $(R_{AP}-R_P)/R_{AP}$} is up to 86%; {i.e., a factor of 7.3 between the parallel (R_P) and antiparallel (R_{AP}) resistance states}; secondly, the switching between these states is extremely sharp $\{R^{-1}(dR/dH)>400\%/\mathrm{Oe}\}$. The distinct binary resistance states and switching points in the $R(H)$ curves, which were stable and reproducible for both magnetic history and thermal cycles, are qualitatively different from any previous magnetic tunnel junction. The reproducible TMR values are higher, and have been achieved at a much higher temperature, than in any previous device. As shown in Fig. 2(b) all the devices on the same chip show similar TMR magnitudes and identical values of the lower coercive field H_{cl}; this value agrees well with the coercive field of a plain LCMO film measured using a superconducting quantum interference device (SQUID) magnetometer. This suggests that H_{cl} is associated with the switching of the common base electrode, whereas devices whose top electrodes are of different sizes and aspect ratios show different values of the higher coercive field. The coherent switching in the R-H curve was qualitatively unaltered by varying the field direction in the plane of the substrate, although the variation of the coercive fields indicates in-plane anisotropy.

It is notoriously difficult to prove tunneling unambiguously.[5] However, the dynamic conductance versus voltage for R_P and R_{AP} states at different temperatures, shown in Fig. 3, can be accurately fitted by Simmons' model.[12] Irrespective of area, the antiparallel barrier resistance area product at 77 K was between 2×10^{-6} and $4\times10^{-5}\ \Omega m^2$.

The temperature dependence of the resistance and TMR is presented in Fig. 4. By 100 K, the TMR is suppressed to about 40% and a measurable TMR disappears above 150 K, although the coherent field switching of the resistance state persists whilst there is a measurable MR. A decrease of TMR with increasing temperature is universal in all magnetic tunneling junction systems, but appears particularly drastic in manganite half metallic systems.[5] From 120 to 300 K the temperature dependence of the junction resistance indicates the development of an activated nontunneling conductance which we attribute to the presence of defective states in the $NdGaO_3$ barrier. However the significant change of the TMR occurs below 120 K where shunting alone cannot explain the temperature dependent junction resistance.

A convincing model for spin tunneling was first formulated by Julliè̀re.[13] This model is based only on the effective

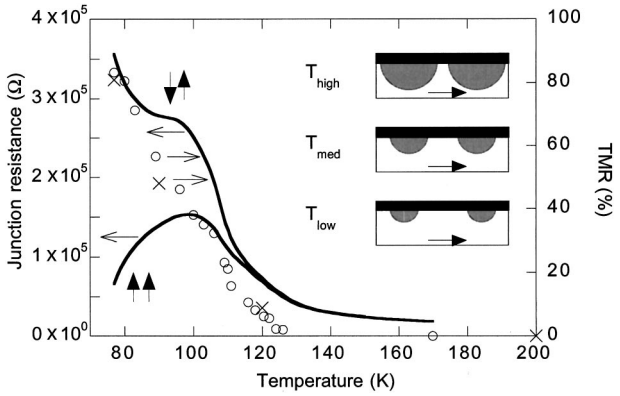

FIG. 4. The temperature dependence of the junction resistance in parallel (1000 Oe) and antiparallel (350 Oe) spin configurations (continuous lines) and the corresponding temperature dependent tunnel magnetoresistance for two different junctions (symbols). The inset schematically illustrates the growth, with decreasing temperature, of interconnected ferromagnetic regions (unshaded) next to the tunnel barrier (black).

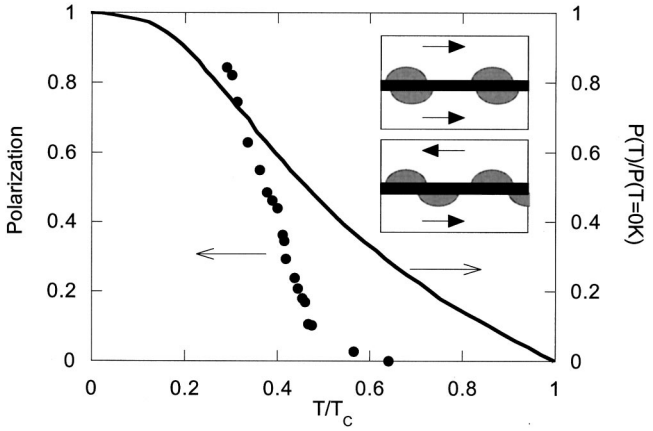

FIG. 5. The temperature-dependent polarization derived from the observed TMR using Eq. (2) is compared to the spin anisotropy of a $La_{0.7}Sr_{0.3}MnO_3$ thin film measured by spin-polarized photoemission (reproduced from Ref. 16). The inset shows a schematic diagram of the tunnel device with phase separated paramagnetic regions adjacent to the barrier shaded gray. The ferromagnetic regions (unshaded) merge further into the electrodes as the effective local T_C rises.

spin polarization at the Fermi energy (E_F) so that for identical electrodes the zero bias conductance is given by

$$R_P^{-1} = M(D_\uparrow^2(E_F) + D_\downarrow^2(E_F)),$$

$$R_{AP}^{-1} = 2MD_\uparrow(E_F)D_\downarrow(E_F), \tag{1}$$

where R_P and R_{AP} are the resistances in parallel and antiparallel orientations, $D_\uparrow(E)$ and $D_\downarrow(E)$ are the spin-up and spin-down density of states and M is the tunneling probability. Thus the TMR is given by

$$\Delta R/R_{AP} = (R_{AP} - R_P)/R_{AP} = 2P^2/1 + P^2, \tag{2}$$

where P is the spin polarization given by $P = (D_\uparrow(E_F) - D_\downarrow(E_F))/(D_\uparrow(E_F) + D_\downarrow(E_F))$.

Using Eq. (2), we plot the apparent polarization as a function of temperature in Fig. 5. The maximum polarization in the LCMO electrodes from the data in Fig. 2 was 0.86. Although the band structure of $La_{1-x}Ca_xMnO_3$ has been calculated and predicted to be essentially half-metallic at low temperatures[2,3,14] our value is very much higher than has been reported for manganite tunnel junctions at this temperature (a maximum of 20–30 %).[4–7] In Fig. 5 we also show the polarization measured by Park *et al.* by spin polarized photoemission.[15,16] Their data is normalized to the low temperature value, and so the curve represents an upper bound to the actual polarization. From the figure it is evident that the two curves cross, and that in the lowest temperature range to which we could measure, our value is unexpectedly above even this upper bound. Indeed, our inferred spin polarization at 77 K is more than the value of 78–80 % in $La_{0.7}Sr_{0.3}MnO_3$ measured directly by Andreev reflection at 4.2 K by Soulen *et al.*[8] and Osofsky *et al.*[17]

This high value must partly be a consequence of the improved structural perfection of our devices; however, the full explanation must be more complicated. Transport measurements of manganite thin films suggest a reduced T_C associated with lattice mismatch and the existence of an electrically dead surface layer.[18] However, our magnetic measurements of LCMO thin films and multilayers on $SrTiO_3$ (Ref. 9) demonstrate that within such dead layers there are regions which are highly ordered, but that these regions must be electrically discontinuous. This spatial inhomogeneity is reminiscent of the phase separation[19] for which there is direct evidence in a number of manganite systems.[20,21] In a tunnel junction, since significant tunneling can only occur between metallic magnetically ordered regions, the extent and distribution of the ferromagnetic regions will critically affect the total tunnel current. Static conductivity contrast images of strained LCMO films by Fäth *et al.*[21] have shown that metallic regions grow both with decreasing temperature and increasing field, nevertheless some insulating regions still persist at low temperatures.

Here we therefore suggest an active tunneling mechanism based on percolative phase separation playing a dominant role accounting for the general TMR temperature dependence in these materials and the high spin polarization in particular. Significant tunneling (and hence MR) will only occur with the growth of the ordered ferromagnetic surface phase; this is illustrated schematically in the inset to Fig. 4. Since the parallel tunnel configuration has a low resistance area product, the percolative growth of FM regions provides an immediate explanation of the rapid fall in R_P with decreasing temperature beyond a certain threshold temperature of around 100 K. Since the degree of strain, and hence surface T_C suppression, is much smaller in our devices with $NdGaO_3$ barriers, one would expect generally higher MR values than with $SrTiO_3$.

The inhomogeneous magnetic state in both electrodes of a tunnel junction raises the question of their mutual alignment. If the relative alignment of the FM regions across the barrier were sensitive to the macroscopic magnetic alignment of the electrodes, then the effective area of the junction would be different in the parallel and antiparallel states; a larger effective tunnel area when the moments were aligned would enhance the MR and hence the inferred polarization could be substantially increased—as we observe in our experiments. This is clearly particularly critical at high temperatures when

the FM area is relatively small, and provides a further reason for the rapid delay in MR with increasing temperature. However, to clarify this in more detail, further experiments on phase separation including the dynamics of the inhomogeneous metal-insulator and magnetic transition will be needed.

This report shows that TMR in half-metallic systems can be qualitatively different in materials systems with optimized interfaces. We have proposed that phase separation at interfaces can provide an explanation for the rapid decay in MR in manganite tunnel junction and a reason why using a better lattice matched insulator dramatically improves the properties. These results raise the possibility of very high TMR in well-engineered half-metallic systems through the control over the scale and alignment of phase separated magnetic regions within devices.

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