Localized reversible nanoscale phase separation in 
Pr$_{0.63}$Ca$_{0.37}$MnO$_3$ single crystal using a scanning tunneling 
microscope tip

Sohini Kar$^*$
Department of Physics, Indian Institute of Science, Bangalore 560 012, India.

A. K. Raychaudhuri$^†$
S.N.Bose National Centre for Basic Sciences, Salt Lake, Kolkata 700 098, India

Abstract
We report the destabilization of the charge ordered insulating (COI) state in a localized region of Pr$_{0.63}$Ca$_{0.37}$MnO$_3$ single crystal by current injection using a scanning tunneling microscope tip. This leads to controlled phase separation and formation of localized metallic nanoislands in the COI matrix which have been detected by local tunneling conductance mapping. The metallic regions thus created persist even after reducing the injected current to lower values. The original conductance state can be restored by injecting a current of similar magnitude but of opposite polarity. We thus achieve reversible nanoscale phase separation that gives rise to the possibility to “write, read and erase” nanosized conducting regions in an insulating matrix with high spatial resolution.

$^*$ electronic mail:sohini@physics.iisc.ernet.in
$^†$ On lien from Department of Physics, Indian Institute of Science, Bangalore 560 012, India; electronic mail: arup@bose.res.in
Rare-earth manganites having the perovskite structure $R_{1-x}A_x$MnO$_3$, where $R$ is a rare earth ion and $A$ is a divalent alkaline-earth ion, have been studied in great detail for the rich variety of distinct phases they exhibit. Of particular interest is the charge ordered insulating (COI) phase which is found to be unstable under various external perturbations such as magnetic field, electric field and current (effects of which are also observed in manganites which are not charge ordered and also by size reduction to few tens of nanometers). Normally, the phase that is created by destabilization of the COI phase is the ferromagnetic metallic (FMM) ground state. Thus these materials are attractive candidates for various switching and sensing devices. The creation of FMM filaments in a bulk single crystal of a COI manganite by using a high current has been shown before. In the present experiment, we demonstrate localized destabilization of the COI phase by current injection using a scanning tunneling microscope (STM) tip over a small area with size $\approx 25 – 30$nm. This phenomenon gives rise to the possibility of patterning (writing) nanosized metallic regions by controlled phase separation on an otherwise insulating background. This process can be reversed (erased) and the metallic region can be switched back to the COI state at will by passing a current of reverse polarity and comparable magnitude to the writing current. Hence, we are able to achieve reversible and controlled phase separation over nanoscopic length scales without altering the topography or structure of the surface.

The sample used in our experiments was a single crystal of Pr$_{0.63}$Ca$_{0.37}$MnO$_3$ (PCMO) grown by float zone technique. The sample has been well characterized and shows a CO transition at $T_{CO} = 235$K. The variable temperature ultra-high vacuum STM used was constructed in our laboratory and we used an SPM100 controller (RHK Technology Inc., USA). The STM was pumped to a base pressure of better than $1 \times 10^{-8}$ Torr after which cryopumping takes over. The STM tips were mechanically formed Pt/Rh (87:13) wires. The crystal was freshly broken to create a clean surface for STM measurements.

In the COI phase, there exists a gap in the charge excitation spectra ($\Delta$). The gap collapses when the COI state is destabilized into a metallic state as has been shown in magnetic field induced destabilization. We first measured $\Delta$ through scanning tunneling spectroscopy (STS). The tunnel current was stabilized at 1nA at a bias of 0.7V. The bias was then swept between $\pm 0.75$V and the tunnel current-voltage ($I-V$) spectra were recorded. The $dI/dV - V$ curves were evaluated from the tunneling spectra and $\Delta$ was evaluated taking into consideration the finite temperature effect. In figure 1, we show $\Delta$ as a function...
FIG. 1: The CO gap ($\Delta$), as a function of temperature. The inset shows an example of the tunneling spectra ($dI/dV - V$) taken at 1nA and 4nA at 152K showing the collapse of the CO gap at higher tunnel current.

The CO temperature can be clearly identified from the temperature dependence of the gap. Above $T_{CO}$ the gap is $\approx 0.05eV$, as is generally observed in the polaronic insulating states of other manganites. We then measured $\Delta$ for higher tunnel currents in a step by step process by bringing the tip closer to the sample. Higher tunnel currents were stabilized at the same point for the same bias and the $I - V$ spectra were recorded again. This process was repeated for various tunnel currents and the $dI/dV - V$ curves were evaluated from the tunneling spectra. It was found that the gap decreases linearly with increasing tunnel current. The higher tunnel currents thus reduce the CO gap leading to destabilization of the CO state, as can be seen from the inset of figure 1 where we show the $dI/dV - V$ curves taken at 152K for tunnel currents of 1nA and 4nA. The destabilization typically occurs around a tunnel current of 4-5nA. This information is important and is used in deciding the “write-read-erase” cycle as will be shown below.

The above observation enables us to use an STM tip to selectively destabilize a given CO region thus controlling spatially the region that one would like to drive metallic in a COI matrix. We refer to this as the “writing” process. We demonstrate this in fig 2 where we have carried out local tunneling conductance mapping (LCMAP) over a given area at $T = 152K$ ($T < T_{CO}$). The LCMAP technique generates a two-dimensional map of the tunneling conductance across the surface for a fixed bias and at a fixed average tunnel current. This is achieved by applying a small ac bias modulation over the dc sample bias and using a lock-in amplifier to measure $dI/dV$ directly. One can simultaneously record topography as
well as the LCMAP of the same area. Fig 2(a) shows the LCMAP of a 100nm×100nm area of the surface of PCMO, taken at a tunnel current of 1nA. We then zoomed into an area marked by the arrow and scanned an area of 25nm×25nm using a tunnel current of 5nA. This was the “writing” cycle. We then zoomed out to the original 100nm×100nm scan area and recorded the LCMAP again with a tunnel current of 1nA. This was the “read” process that established whether the chosen region has become more conducting. As can be seen from fig2(b), there is a square area of about 30nm×30nm which has significantly higher tunnel conductance than the surrounding region. In our color scheme, the higher tunneling conductance region appears brighter. The brighter region has a conductance that is typically ≈ 3 times higher than the surrounding darker region. (The surrounding region is not uniformly dark and has small bright pockets that already existed in the pristine single crystal.)

To “erase” the conducting region created in the above process, we injected a current of comparable magnitude but of opposite polarity. We zoomed back into the 25nm×25nm spot that was written before and scanned the same area again using -5nA tunnel current. When we recorded the zoomed out image at 1nA again, we found that we had managed to erase the metallic region almost completely thus reverting it back to a region of low tunneling conductance, as can be seen in fig 2(c). This is a very important observation as this phenomenon can be used to selectively write, read and erase nanosized metallic domains (regions of high tunnel conductance) in an insulating background (regions of lower tunneling conductance) using an STM tip. The small region of high conductance marked with an arrow in figure 2(a) was used as a marker, so that when the erase process was done one could see that the region had almost reduced to the original size. The conductance of the starting marker patch was about 5.9nA/V(fig 2(a)) and after the erasing the conductance of the marker patch is 6.4nA/V. (fig 2(c)). We note that in this process the topography had not changed.

We then carried out STS measurements to establish that the nano-island created was a metallic region with no CO gap (\(\Delta \to 0\)). After the write process, we took tunneling spectra at different points on the surface that included the written region as well as the pristine regions. We found two distinct \(I-V\) curves as shown in figure 3. The inset shows the corresponding \(dI/dV-V\) curves. One set of \(I-V\) curves taken on the “written” region shows metallic behavior with no gap (\(\Delta \approx 0\)) while the other set taken on the virgin regions
FIG. 2: Collection of LCMAPs taken at 152K showing selective electronic phase transition in PCMO single crystal. (a) LCMAP of 100nm×100nm area taken at 1nA, (b) LCMAP of the same area taken at 1nA tunnel current, after scanning a 25nm×25nm area near the center with tunnel current of 5nA and (c) LCMAP of the same area taken at 1nA after scanning an area of 25nm×25nm at the center with -5nA tunnel current. (The small thermal drift is not corrected.)

FIG. 3: Two distinct kinds of $I-V$s showing both metallic (squares) and insulating phases (circles). The coexisting phases were created after injecting a large tunnel current (5nA). The inset shows the corresponding $dI/dV-V$ curves.

shows a finite gap ($\Delta \neq 0$) opening up in the tunneling spectra. This shows that we have two distinct phases coexisting, the COI phase with a finite gap and the metallic region where a high tunnel current had been injected.

To investigate whether we can create controlled phase separation over a larger area, we carried out LCMAP measurements over a 75nm×75nm area. To start with, we scanned the entire area at a tunnel current of 1nA and bias of 200mV and recorded the LCMAP (fig 4(a)). We then increased the tunnel current to 5nA and scanned the entire area at this higher tunnel current. We then reduced the tunnel current back to 1nA and recorded the LCMAP taken over the same area, shown in figure 4(b). We find that, in this case, the LCMAP is brighter, that is, some regions have become more conducting upon passing
FIG. 4: Collection of LCMAPs taken at a tunnel current of 1nA over a 75nm×75nm area, (a) before scanning the area with 5nA (b) after scanning with 5nA and (c) after having scanned the area with a tunnel current of -5nA.

a tunnel current of 5nA. This implies that by scanning the area at 5nA, the average local tunneling conductance has increased and this enhanced conductance state is retained even over a larger area. We then reversed the tunnel current and scanned the same region with -5nA and then recorded the LCMAP with a tunnel current of 1nA again. Interestingly, this flipping of tunnel current erases the enhanced conductance and we return to our original starting point as can be seen in fig 4(c). We find that in general the creation of regions of higher conductance over a larger area is not homogeneous and these regions are created generally at steps on the crystal surface. It is not clear why the preferential destabilization of the COI state occurs at the steps, however, it may happen that the charge ordering itself is spatially inhomogeneous and these regions of the crystal surface make them weaker spots where the destabilization can be initiated.

It should be noted that the underlying topography of the single crystal surface makes this process somewhat difficult to observe over larger length scales as most of the contrast in the LCMAP can sometimes be masked due to the inhomogeneity of the surface. The experiment in principle can be better done on an epitaxial film. However, the strain in such films affects the charge ordering and can initiate phase separation.

We note that the write-read-erase cycle can be done repeatedly and also one can reverse the polarity to achieve the same cycle; that is, one can destabilize the charge ordering with a large negative tunnel current and subsequently restore it using a tunnel current of the opposite polarity but having roughly the same magnitude. This establishes that the direction of the tunnel current is not important in this process.

One particular issue that this experiment can address is whether the phenomenon is driven by current injection or is due to field effect. We argue that it is current injection driven. Firstly, since the tunnel junction has much higher resistance (∼100MΩ or more)
than the sample, most of the voltage drop occurs across the tunneling gap and there is no significant voltage drop within the sample that can give rise to the observed phenomenon. Secondly, if the phenomenon is due to a field effect, it would have depended on the polarity, since this would decide whether the concentration of holes or electrons was increasing. It is known that charge ordering is strongest in the $x = 0.5$ composition. Thus, in our sample where $x = 0.37$, a negative bias would imply injection of holes which should drive the system towards the $x = 0.5$ range, making the charge ordering stronger. Thus destabilization of the COI state would not have been possible. A positive bias would lead to the opposite effect. However, we find that regardless of the sign, a higher tunnel current always destabilizes the charge ordering leading to formation of the metallic region. In conclusion, we establish that current injection through an STM tip can give rise to controlled phase separation thus creating metallic nanoislands in a COI. This observation raises the possibility of information storage in COI materials by tunnel current injection.

S.K. thanks CSIR, Government of India, for a fellowship. A.K.R. thanks DST, Government of India, for a sponsored project.
1 Colossal Magnetoresistance, Charge Ordering and Related Properties of Manganese Oxides, edited by C.N.R. Rao and B. Raveau, (World Scientific, Singapore, 1998) and Colossal Magnetoresistive Oxides, edited by Y. Tokura (Gordon and Breach Science, Singapore, 2000).

2 E. Dagotto, T. Hotta and A. Moreo, Phys. Rep., 344, 1 (2001).

3 H. Kuwahara, Y. Tomioka, A. Asamitsu, Y. Moritomo and Y. Tokura, Science, 270, 961 (1995).

4 A. Guha, N. Khare, A. K. Raychaudhuri and C. N. Rao, Phys. Rev. B., 62, R11941 (2000).

5 A. Asamitsu, Y. Tomioka and Y. Tokura, Nature (London), 388, 50 (1997).

6 H. Jain, A. K. Raychaudhuri, Ya. M. Mukovskii and D. Shulyatev, Appl. Phys. Lett., 89, 152116 (2006).

7 T. Wu, S. B. Ogale, J. E. Garrison, B. Nagaraj, A. Biswas, Z. Chen, R. L. Greene, R. Ramesh, T. Venkatesan and A. J. Millis, Phys. Rev. Lett., 86, 5998 (2001).

8 J. Gao, S. Q. Shen, T. K Li and J. R. Sun, Appl. Phys. Lett., 82, 4732 (2003).

9 C. H. Ahn, J. -M Triscone and J. Mannhart, Nature, 424, 1015 (2003).

10 T. Sarkar and A. K. Raychaudhuri, J. Appl. Phys., 101, 124307 (2007).

11 A. Biswas, A. Arulraj, A. K. Raychaudhuri and C. N. R. Rao, J. Phys. D: Condens. Matter, 12, L101 (2000).

12 S. Kar, J. Mitra and A. K. Raychaudhuri, Solid State Commun., 270, 961 (2005).