Electric-field-induced insulator–metal transitions in thin films of charge-ordered rare-earth manganates

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Thin films of charge-ordered $Nd_{0.5}Ca_{0.5}MnO_3$, $Y_{0.5}Ca_{0.5}MnO_3$, and $Nd_{0.5}Sr_{0.5}MnO_3$ have been prepared on Si(100) and $LaAlO_3$(100) substrates by the nebulized spray pyrolysis of organometallic precursors. Small electric fields induce insulator–metal transitions in the films with the resistivity decreasing with increasing current. The current–voltage characteristics are non-ohmic and show some hysteresis. The current-induced negative differential resistance found in these manganate films could have potential technological applications. © *1999 American Institute of Physics.* [S0003-6951(99)01402-3]

Rare-earth manganates of the formula $Ln_{1-x}A_xMnO_3$ (where Ln=rare earth, A=alkaline earth) exhibit important phenomena such as colossal magnetoresistance (CMR) and charge ordering.[1,2] Charge ordering in the manganates is especially interesting because it competes with double exchange, giving rise to interesting properties. Charge ordering is favored in certain compositions such as those with $x=0.5$ and is associated with insulating behavior and in certain instances, antiferromagnetism as well. Two types of charge ordering can be distinguished in the manganates.[3] In manganates such as $Nd_{0.5}Sr_{0.5}MnO_3$ with a relatively large average radius of the A site cations $\langle r_A \rangle$, a ferromagnetic metallic (FMM) state ($T_c=250$ K) transforms to a charge-ordered (CO) state on cooling to ~150 K.[4] Manganates with a small $\langle r_A \rangle \lesssim 1.17$ Å, do not exist in the FMM state at any temperature, but instead are charge ordered at relatively high temperatures. The CO state in a manganate with a relatively large A site ion radius ($\langle r_A \rangle \gtrsim 1.17$ Å) can be transformed to the FMM state by the application of magnetic fields. On the other hand, even large magnetic fields ($\gtrsim$40 T) have a negligible effect on the CO state of $Y_{0.5}Ca_{0.5}MnO_3$ with a $\langle r_A \rangle$ of 1.13 Å. The CO state in single crystals of $Pr_{1-x}Ca_xMnO_3$ has been transformed to the FMM state by applying electric fields or by laser irradiation.[5,6] An examination of the literature shows that there has been little or no effort to prepare thin films of the charge-ordered manganates, although thin films of the manganates showing CMR have been prepared by various means.[7–10] In this letter, we report the successful preparation of thin films of the charge-ordered manganates, $Nd_{0.5}Ca_{0.5}MnO_3$(NCM), $Y_{0.5}Ca_{0.5}MnO_3$(YCM), and $Nd_{0.5}Sr_{0.5}MnO_3$(NSM) on single crystal substrates by employing nebulized spray pyrolysis of organometallic precursors. More importantly, we have investigated the electric current-induced transition from the insulating CO state to the metallic state in these films. It is noteworthy that the insulator–metal transition in the thin films of the CO manganates is brought about by passing small currents. Even YCM with a very small $\langle r_A \rangle$ exhibits this phenomenon although high magnetic fields have no effect on the CO state in this material.

Thin films of the manganates were deposited on Si(100) as well as on LaO(100) single crystal substrates by employing nebulized spray pyrolysis.[11] This technique involves the pyrolysis of a nebulized spray of organic derivatives of the relevant metals. Since the nebulized spray is deposited on a solid substrate at relatively low temperatures, and with sufficient control of the rate of deposition, the oxide films obtained possess good stoichiometry. Employing acetylacetonates of Nd, Ca, and Mn and dipivaloylmethanato strontium as the organometallic precursors, films of ~1000 nm thick-

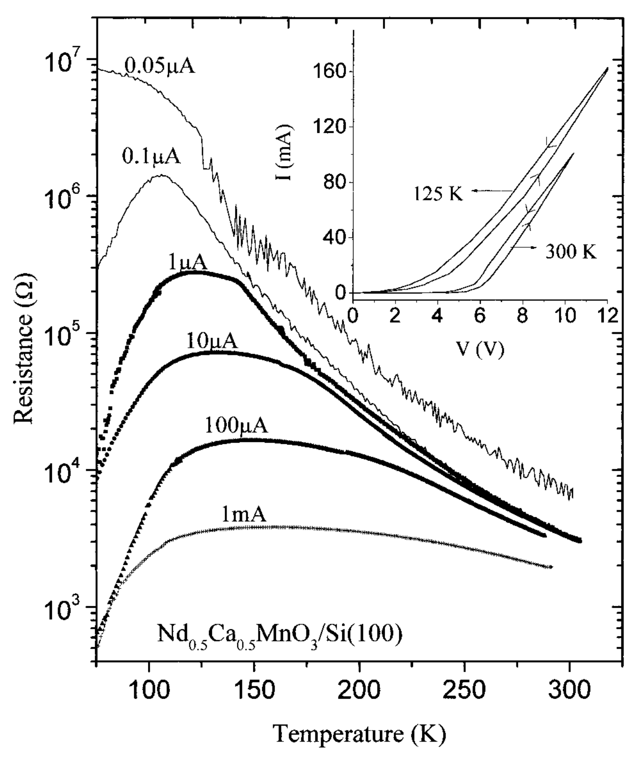

FIG. 1. Temperature variation of the resistance of a polycrystalline $Nd_{0.5}Ca_{0.5}MnO_3$ film deposited on Si(100) for different values of current. Inset shows $I-V$ characteristics at two temperatures.

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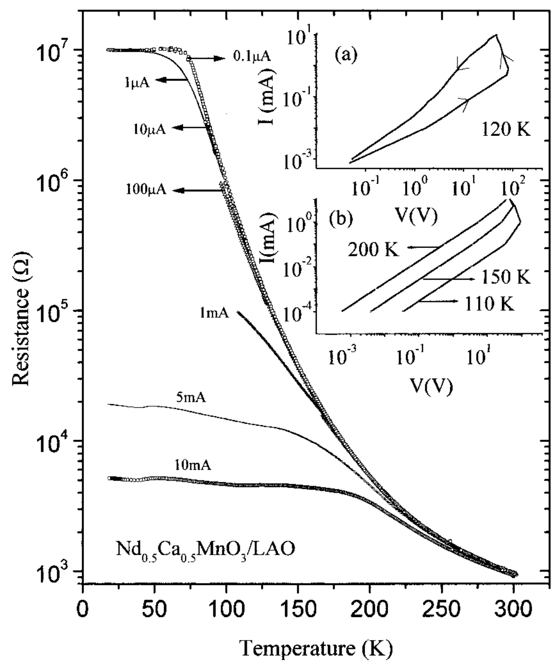

FIG. 2. Temperature variation of the resistance of an oriented $Nd_{0.5}Ca_{0.5}MnO_3$ film deposited on $LaAlO_3(100)$ for different values of current. Insets show $I-V$ curves demonstrating (a) hysteresis and (b) non-ohmic behavior.

ness were deposited at 650 K by using air as the carrier gas (1.5 ℓ/min). The films so obtained were heated at 1000 K in oxygen. These films were characterized by employing x-ray diffraction and scanning electron microscopy. The compositions of the films as determined by energy dispersive analysis

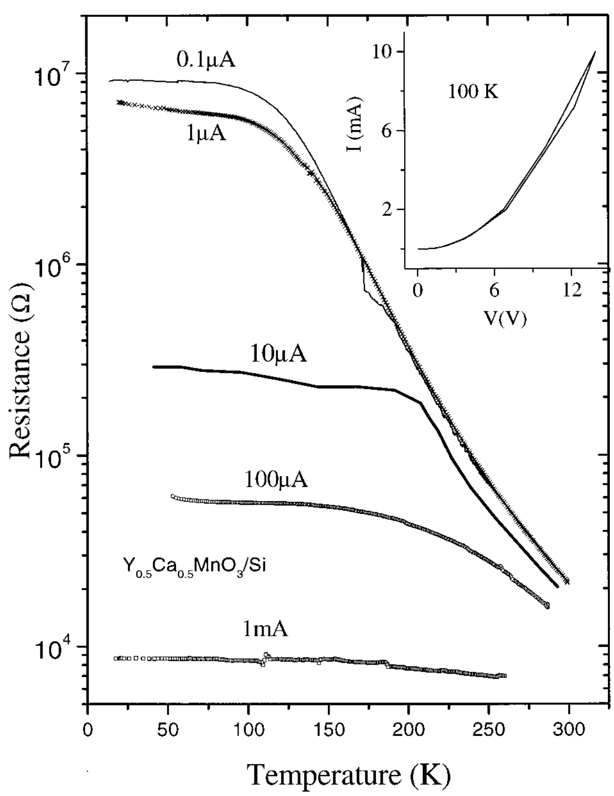

FIG. 3. Temperature variation of the resistance of a polycrystalline $Y_{0.5}Ca_{0.5}MnO_3$ film deposited on Si(100) for different values of current. Inset shows $I-V$ characteristics at 100 K.

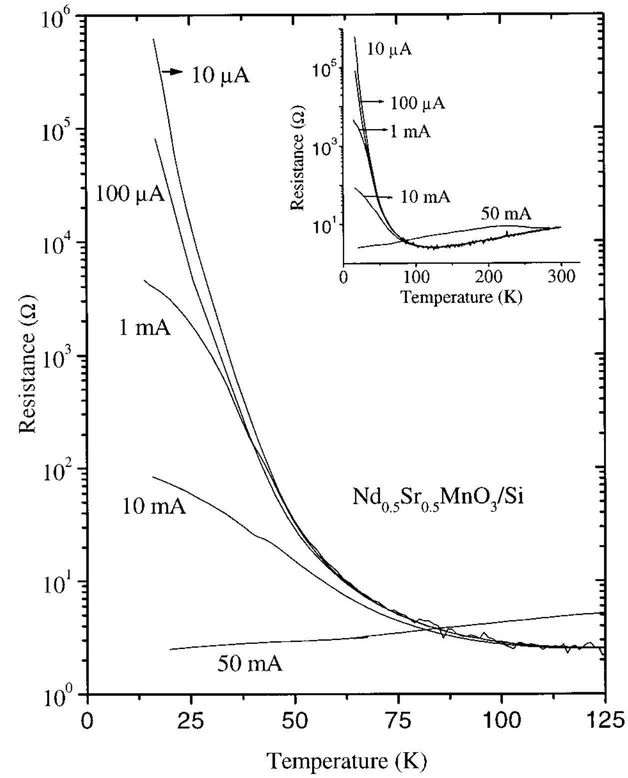

FIG. 4. Temperature variation of the resistance of a polycrystalline $Nd_{0.5}Sr_{0.5}MnO_3$ film deposited on Si(100) for different values of current. Inset shows data over a wide temperature range.

by x rays (EDAX) were close to the stated compositions. The films deposited on Si(100) showed polycrystalline nature while those deposited on LaO were oriented along the (100) direction. The orthorhombic lattice parameters of the materials agree with the literature values. Temperature-dependent resistivity measurements were carried out by employing close cycle refrigerator and sputtered gold electrodes.

In Fig. 1 we show the temperature variation of resistance of a polycrystalline NCM film deposited on Si(100), for different values of the dc current passed. With a current of 0.05 μA, the film shows the known insulating behavior of NCM. With increasing current, however, we see the definitive occurrence of an insulator–metal ($I-M$) transition. It is noteworthy that even a current of 0.1 μA causes the $I-M$ transition. It was ascertained that the observed effects were not due to local heating. Local heating effects became apparent only at higher current values ($\geqslant$50 mA). The temperature of the $I-M$ transition shifts from 100 to 150 K with increase in current. The current–voltage ($I-V$) curves show non-ohmic behavior with some hysteresis, as shown in the inset of Fig. 1. Measurements on the highly oriented NCM film deposited on LaO also show the negative differential resistance (Fig. 2), with the resistance decreasing markedly with increasing current. We do not clearly see a metal-like decrease in resistance at low temperatures, and the behavior is similar to that in the $I-M$ transition of laser-irradiated $Pr_{1-x}Ca_xMnO_3$ crystals reported by Ogawa *et al.*[6] The oriented NCM films also show non-ohmic behavior and hysteresis as shown in the insets in Fig. 2.

In Fig. 3 we show the resistance versus temperature curves for a YCM film on Si(100) for different values of the current. We observe a substantial decrease in resistance with the increase in current in YCM as well and the $I-V$ behavior is non-ohmic. The occurrence of a current-induced $I-M$ transition in YCM is indeed noteworthy as the CO state in this material is very robust, being unaffected by magnetic fields or substitution of Mn^{3+} by Cr^{3+} and such ions.[12]

In Fig. 4 we show the temperature variation of resistance of a NSM film deposited on Si(100). NSM shows metallic behavior from ~300 K and an increase in resistance at low temperatures due to charge ordering. The increase in resistance in the CO state is not as sharp in the film as in a single crystal.[13] However, we see that the high-temperature metallic behavior is found for all current values, but the resistance decreases substantially in the charge ordering regime, with the increase in current. At 50 mA, the material remains metallic from 300 to 20 K, although there is a slight heating of the sample at this current value.

The electric current-induced negative differential resistance behavior found in the rare-earth manganate films probably involves a special type of dielectric breakdown of the charge-order state, brought about by small electric fields. It seems likely that the barrier between CO and the metallic state is not very large since a small electric field can cause such a $I-M$ transition. The passage of current may generate a conduction path giving rise to metallic characteristics and the localized and metallic electron states could then coexist with independent channels for conduction, just as in the case of charge density wave systems.[14] The electric-field-induced $I-M$ transitions in the rare-earth manganate films described here may have potential technological applications in switching and other devices.

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