Electrical transport between epitaxial manganites and carbon nanotubes

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The possibility of performing spintronics at the molecular level may be realized in devices that combine fully spin polarized oxides, such as manganites with carbon nanotubes. However, it is not clear whether electrical transport between such different material systems is viable. Here, we show that the room-temperature conductance of manganite-nanotube-manganite devices is only one-half of the value recorded in similar palladium-nanotube-palladium devices. Interestingly, the former shows a gap in the conductivity below the relatively high temperature of 200 K. Our results suggest the possibility of new spintronics heterostructures that exploit fully spin polarized sources and drains. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2170431]

Spin devices are one of the most sought after elements for the electronics of tomorrow. These devices aim to exploit the spin degree of freedom of the electron, in order to achieve new functionality with respect to conventional electronics. A range of effects has been observed in suitable materials and heterostructures. For example, giant magnetoresistance (MR) is seen in metallic multilayers,[1] and tunneling MR is seen in magnetic tunnel junctions.[2] These examples exploit the fact that ferromagnets possess spin-polarized electrons. The magnitude of the MR increases when the spin polarization (P) of the ferromagnetic layers is increased,[3] where P is defined to be the relative difference between the populations of spin-up and spin-down conduction electrons. This has been investigated experimentally with materials, such as Fe_3O_4, CrO_2 and, more extensively, mixed-valent manganites such as $La_{0.7}Ca_{0.3}MnO_3$.[4–7] These compounds have all been argued[8] to be half-metallic ($P=100\%$) at low temperatures, such that the minority carrier band is empty. If we consider that Co is the best elemental ferromagnet with $P=45\%$,[9] then we can understand the advantage of building spin devices from half-metallic materials.

In parallel with these developments in spintronics, the ever-increasing drive toward miniaturization in the semiconductor industry has delivered devices with characteristic length scales that are comparable to the dimensions of some organic molecules.[10] To go beyond the silicon roadmap,[11] there have been many recent efforts to integrate molecules into electronic circuits. In this molecular electronics approach, many molecules have been tested in order to establish whether they are able to perform basic electronic processes (such as amplification or rectification), or even new and unexpected effects.[12] Out of all possible molecular building blocks, carbon nanotubes (CNTs) are among the most studied and have shown the most promising results.[13] For example, logic gates[14] have been fabricated using room-temperature transistors based on semiconducting single-walled CNTs.[15] Also, ballistic conduction in nanotubes, which leads to extraordinary properties, offers the possibility of faster devices that consume less power.[16]

There have been some attempts at integrating spintronics and molecular electronics: Tsukagoshi *et al.*[17] successfully contacted multiwalled CNTs to ferromagnetic Co contacts, and showed a few percent low-temperature MR effect.[17] Other groups have obtained similar but inconsistent results.[18–21]

Our purpose is to show the possibility of electrically connecting a molecule to a magnetic material that shows full spin polarization. We have chosen to work with CNTs and the most promising half-metallic candidate, i.e., a mixed valent manganese oxide (a manganite).

If electrical conductivity is possible between such different materials systems, then it may be possible to control electronic spin states in CNTs over distances that are long compared with tunnel junction barrier widths of a few nanometers. Moreover, the diameter of a CNT is much smaller than the lateral dimensions of a typical barrier, suggesting improved performance. Thus, one can envisage large MR effects, as well as the creation of extremely localized sources of spin-polarized electrons, for more challenging applica-

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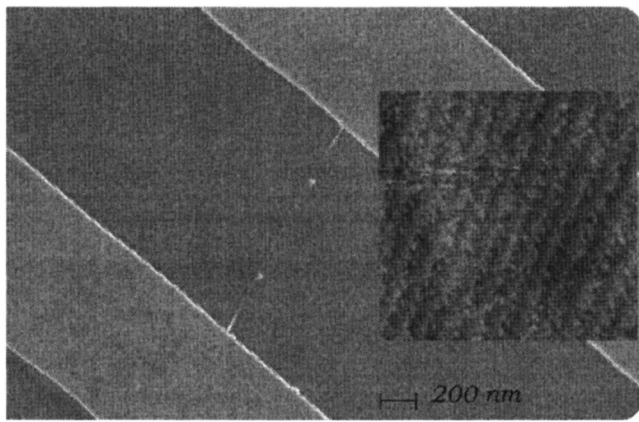
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FIG. 1. Scanning electron microscopy photograph of a multiwalled CNT in electrical contact with two manganite lines that act as electrodes for the LSMO-CNT-LSMO devices. Inset: The 3.7 A terraces that are visible in this AFM picture of the LSMO film prior patterning are evidence of good epitaxy, given that the underlying substrate possesses similar terraces due to the vicinal offcut.

FIG. 2. A typical *I-V* characteristic for Pd-CNT-Pd devices. Inset: A typical *dI/dV* trace showing the development of a zero-bias anomaly at low temperatures.

tions such as quantum computing.[22] From a more fundamental point of view, ferromagnetic contacts may prove a useful probe of spin-charge separation in Luttinger-liquid (LL) materials.[23–25]

High-quality single-crystal films of $La_{2/3}Sr_{1/3}MnO_3$ (LSMO) were grown on commercially available $SrTiO_3$ (001) substrates (Crystal GmbH, Germany) by pulsed laser deposition. Details about the sample growth and morphological characterization can be found elsewhere.[6] This particular manganite composition was chosen because it is fully spin polarized at low temperature[8] and its ferromagnetic properties persist well above room temperature.[26] X-ray diffraction and atomic force microscopy (AFM) showed the films are 30 nm thick and fully strained, with unit cell terraces in the surface.

Pd was chosen as a control electrode material because it combines a high work function with good wetting properties for nanotubes, leading to a low contact resistance.[27] Pd films were grown on $SrTiO_3$ (001) substrates by dc sputtering. The Pd resistivity was found to be 20 $\mu\Omega$ cm at 10 K.

Lines of width 1 μm and separation 1.5 μm were created in the LSMO and Pd films by conventional photolithography and Ar-ion milling. Commercial high-quality multiwalled CNTs (Iljin Nanotech Co., Ltd., Korea) with lengths in excess of 3 μm were dispersed on the patterned chips from an ultrasonicated solution (Fig. 1). A total of nine LSMO and 8 Pd working devices were fabricated.

We now discuss the electrical transport and magnetic properties of the LSMO films prior to patterning. Metallic behavior was seen from room temperature down to the lowest temperature measured, and a residual resistivity of around 50 $\mu\Omega$ cm was recorded at 10 K. Ferromagnetic behavior was seen below a Curie temperature of 360 K, and the low-temperature saturation magnetization is 3.6 μ_B/Mn, just 3% less than the theoretical value of 3.7 μ_B/Mn. Therefore, the manganite films are of the highest possible quality[28] ensuring a high *P*.

We first present results for the Pd-CNT-Pd control devices. Nonlinearity in the current-voltage (*I-V*) characteristics persisted up to room temperature (Fig. 2), and the zero-bias anomaly is clearly enhanced at lower temperatures [Fig. 2 (inset)]. Although we find no sign of blocked conductivity
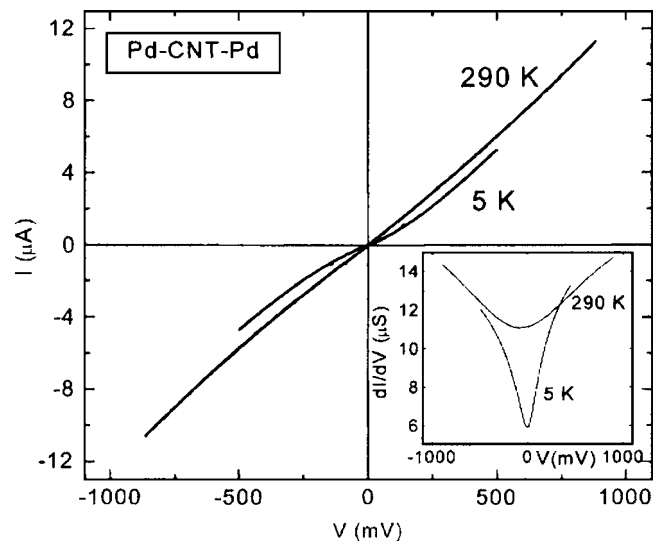
at low bias at the lowest temperature studied (4.2 K), we attribute this to the fact that we only took data down to 4.2 K. The conductance was found to vary with the characteristic power laws $G(T) \propto T^\alpha (eV \ll kT)$ and $G(V) \propto V^\alpha (eV \gg kT)$ with $\alpha \sim 0.4$—not shown. Similar behavior has also been observed in multiwalled CNT-metal samples, and explained using the environmental Coulomb blockade theory.[29] Note that we rule out the possibility of conduction pathways via the substrate, since in similar measurements of Pd lines without CNTs, the current is four orders of magnitude smaller (<0.1 nA at 1 V).

We now turn to our LSMO-CNT-LSMO devices. Our first observation is that all devices measured behave similarly, as do the Pd-CNT-Pd devices. At room temperature, the conductance of the Pd-CNT-Pd devices is around double the conductance of the LSMO-CNT-LSMO devices. Given the resistivities of the device components, the CNT contact resistance in both types of devices (which we cannot measure in our two-point geometry) must dominate. Therefore, the LSMO-CNT contact resistance is roughly double the Pd-CNT contact resistance.

The conductance of the LSMO-CNT-LSMO devices decreases with decreasing temperature, and becomes blocked at ~200 K (Fig. 3). This is a remarkably high temperature compared with typical values (~10 K)[13] (Ref. 13) in nanotube devices. The gap saturates to ~250 meV at very low temperatures (Fig. 4). This blocking energy is remarkably large with respect to typical values (5–25 meV)[13] (Ref. 13) in nanotube devices. At 5 K, the conductance in the high-voltage limit again follows a $G(V) \propto V^\alpha$ power law, but with $\alpha \sim 2.8$ in all samples studied (Fig. 4 inset). This value is far from the value of $\alpha \sim 0.4$ obtained earlier for Pd-CNT-Pd devices, and would imply strong repulsive interactions in LL theory.

The presence of the gap in all of our LSMO-CNT-LSMO devices suggests that interfacial details are independent of the details of at least the outermost nanotube (e.g. diameter, chirality, etc.). For example, in every case, the crystal lattice mismatch could be poor, and the LSMO surface magnetization[30] and thus conductivity suppressed. We note that our device performance is reminiscent of two back-to-
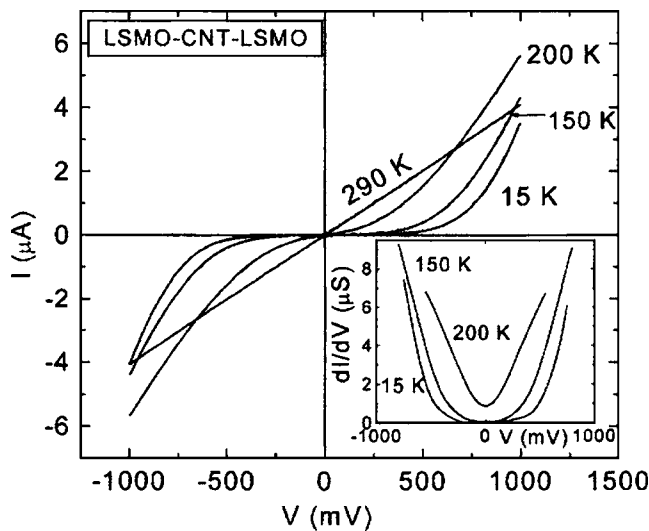
FIG. 3. Typical *I-V* characteristics at different temperatures for the LSMO-CNT-LSMO devices. As the temperature is lowered, a region of blocked conductance appears at low voltages. This can be clearly seen in the *dI/dV* curves (inset).

back Schottky barriers, but the complexities discussed above preclude the standard analysis.

In conclusion, we have established that it is possible to pass an electrical current between a half-metallic oxide and a multiwall CNT. At room temperature, the nanotube contact resistance is only double the value recorded for similar devices with nonmagnetic metallic electrodes made from Pd. Below 200 K, a gap develops in the I-V characteristics and saturates to ~250 meV at very low temperatures. Future device improvements include the use of single-wall nanotubes, the incorporation of a gate electrode to permit the carrier density in semiconducting tubes to be varied, the use of
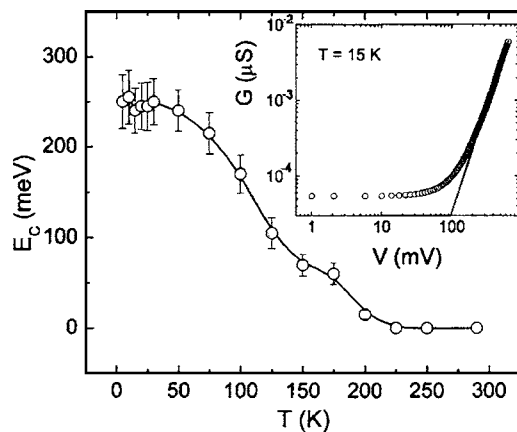
LSMO lines with different widths to achieve different coercive fields, and the use of ultrathin "wetting" layers for reduced contact resistance.

FIG. 4. Estimated values of the blocking energy (E_C) extracted from *dI/dV* for the LSMO-CNT-LSMO devices. The line is a guide for the eyes. Inset: A typical conductance *G* as a function of the applied voltage *V* for the LSMO-CNT-LSMO devices at 5 K. The line represents a power-law fit with $\alpha=2.8$.

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