Magnetic-Field-Dependent Carrier Injection at $La_{2/3}Sr_{1/3}MnO_3$/ and Organic Semiconductors Interfaces

D. Wu,[1] Z. H. Xiong,[1] X. G. Li,[2] Z. V. Vardeny,[1] and Jing Shi[1]

[1]*Department of Physics, University of Utah, Salt Lake City, Utah 84112, USA*

[2]*Hefei National Laboratory for Physical Sciences at Microscale and Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, People's Republic of China*

(Received 8 December 2004; published 1 July 2005)

We have fabricated organic diodes utilizing several π-conjugated organic semiconductors (OSEC) as spacer layers between $La_{2/3}Sr_{1/3}MnO_3$ (LSMO) and various metallic electrodes, and measured their magnetoresistance (MR) and magnetoelectroluminescence (MEL) responses. The devices exhibit large negative high-field MR responses that resemble the MR response of the LSMO electrode, but amplified by ~3 orders in the resistance, and accompanied by a positive high-field MEL effect. These magnetic-field effects result from enhanced carrier injection at the LSMO-OSEC interface that is attributed to the anomalous field-dependent Fermi level shift in LSMO.

DOI: 10.1103/PhysRevLett.95.016802 PACS numbers: 73.43.Qt, 72.15.Gd, 72.20.My, 73.50.Jt

A large spin-valve magnetoresistance (MR) effect was recently discovered in sandwich structures of ferromagnetic (FM) $La_{2/3}Sr_{1/3}MnO_3$ (LSMO) and cobalt (Co) electrodes with a π-conjugated organic semiconductor (OSEC) spacer at low magnetic fields [1]. In that work we also found another large and intriguing MR effect that persisted up to 1 T. A similar effect was previously reported in LSMO-based magnetic tunnel junctions [2] and LSMO-based planar devices with an organic spacer [3]. Whereas the spin-valve MR effect entails coherent spin transport in the OSEC layer [1], the origin of the high-field MR (HFMR) effect is distinctly different due to its unique magnetic-field and temperature dependences, which might be associated with the exotic properties of the LSMO electrode. In the present work we focus on the physical origin of the HFMR effect in OSEC sandwich structures based on LSMO, and show that such devices can be used to study magnetic-field induced changes in the electronic structure of FM electrodes.

We fabricated a variety of organic diode structures, in which the π-conjugated OSEC layer is sandwiched between the LSMO anode and a metal cathode such as aluminum (Al) or Co. Some diodes showed electroluminescence at forward bias voltages, and thus we also measured their magnetoelectroluminescence (MEL) as well as MR. We found that independent of the OSEC layer and temperature, both HFMR and high-field MEL (HFMEL) depend approximately linearly on H. The HFMR is similar to that of the LSMO electrode itself, but amplified by about 3 orders of magnitude in resistance. This strongly indicates that the observed large HFMR and HFMEL effects share a common origin that is related to the magnetic properties of the LSMO electrode, namely, the field-enhanced carrier injection at the LSMO-OSEC interface. By measuring the device current-voltage (I-V) characteristics at different H we show that the LSMO field-enhanced carrier injection can be explained by an anomalous field-induced Fermi level shift. This effect was predicted in double-exchange FM materials, and it originates from the large field-induced change in the Mn e_g-electron bandwidth [4].

The organic diodes were of the form LSMO-OSEC/metal, in which the π-conjugated OSEC layer was either a small molecule, such as 8-hydroxy-quinoline aluminum (Alq_3), N, N′-Di-[(1-napthalenyl)-N,N′-diphenyl]-(1,1′-biphenyl)-4,4′ diamine (NPD), and Alq_3/lithium fluoride (LiF) bi-layer, or a polymer such as polyfluorene (PFO). The bottom LSMO film was about 100 nm thick grown on a $LaAlO_3$ (LAO) insulating substrate using the technique described elsewhere [5]. The top metal electrode can be Co or Al, but the bottom electrode is always *the same LSMO film* [6]. The Alq_3 and NPD small molecule films (~120 nm thick) were deposited by thermal evaporation in a high-vacuum (~10^{-7} torr) chamber, whereas the PFO polymer film (~100 nm thick) was spin coated in a glove box. The top electrode was thermally evaporated following the OSEC layer deposition. All sandwich devices have a ~1 mm × 1 mm active area. The device MR and MEL were measured in a closed-cycle refrigerator equipped with an electromagnet up to 1 T and optical windows, or in a cryostat with a superconducting magnet up to 7 T. The EL emission from the organic light emitting diodes was measured at various H and forward bias voltage V using a Si-photodiode detector and a preamplifier.

We first measured the LSMO film resistance, R vs an in-plane H up to 7 T, over a wide range of temperatures using the two-terminal method. R exhibits the usual negative HFMR characteristic of single crystal films, as found before for epitaxially grown samples [Fig. 1(a)] [7,8]. The HFMR ratio ($\frac{\Delta R}{R} = \frac{R(0\ \mathrm{T}) - R(7\ \mathrm{T})}{R(0\ \mathrm{T})}$) increases from about 20% at low temperatures up to 40% at room temperature, as shown in Fig. 1(b). Since the FM transition temperature $T_c > 300$ K for our LSMO film [1], the pronounced rise of the HFMR ratio at high temperatures is consistent with the

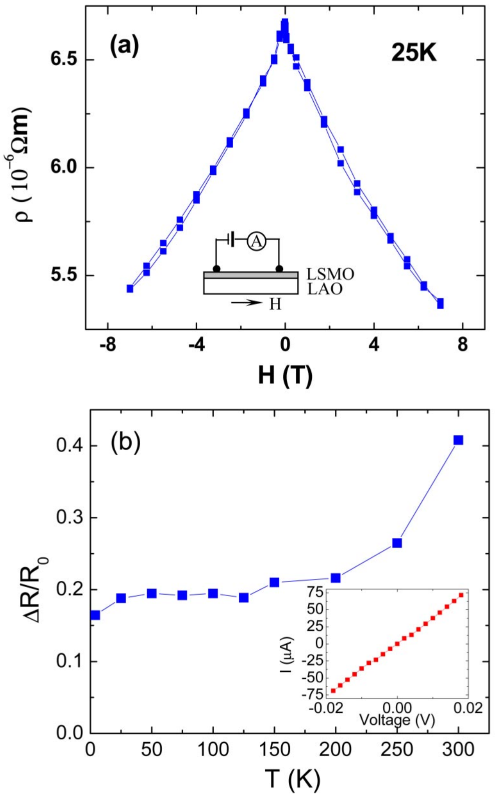

FIG. 1 (color online). (a) In-plane resistivity vs H of an LSMO film at 25 K. (b) MR ratio at $H = 7$ T vs temperature. The inset shows the linear I-V response of the LSMO at 25 K.

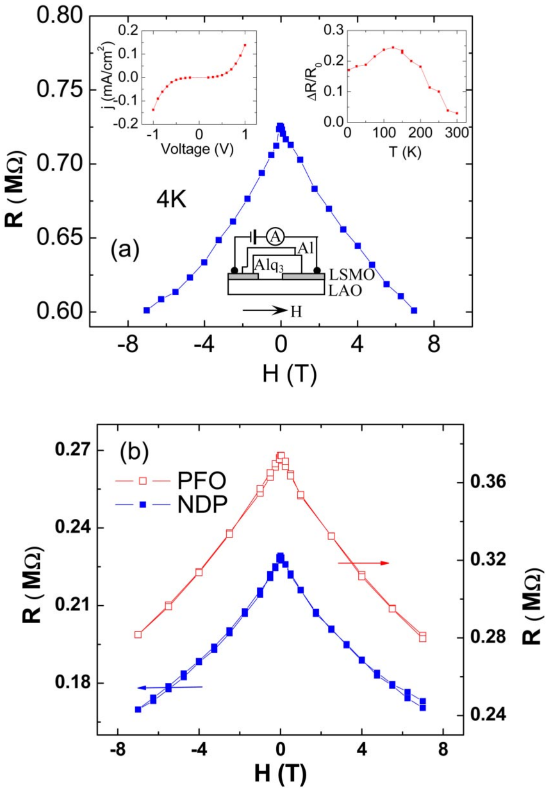

FIG. 2 (color online). (a) Resistance vs H for an LSMO/Alq$_3$(120 nm)/Al diode at 4 K and bias voltage 1 V. The left inset is its nonlinear I-V response, and the right inset is the MR ratio vs temperature at 7 T and 0.7 V. (b) Resistance vs H for an LSMO/PFO/Al diode at 4 K and 0.4 V, and LSMO/NPD(120 nm)/Al at 150 K and 0.3 V.

behavior of other colossal magnetoresistive materials. The temperature dependence of the resistance [i.e., positive $dR(T)/dT$ (not shown)], and the Ohmic I-V characteristic [Fig. 1(b) inset] are typical of metallic behavior, which is expected for double-exchange FM metals such as $La_{1-x}Sr_xMnO_3$ for $0.2 < x < 0.5$.

We previously found in LSMO/Alq$_3$/Co structures that the MR effect consists of two components. At low fields ($H < 300$ Oe), switching the magnetization directions of the FM electrodes caused a spin-valve MR effect. R in the parallel magnetization configuration was measured to be higher than R in the antiparallel magnetization configuration [1]. In the high field region ($H > 500$ Oe) where the magnetization directions of the two FM layers are already switched into the parallel alignment, a higher magnetic field would only further align the magnetizations, and consequently would increase the resistance. However, we found instead that R in these devices steadily decreases with H, and this strongly suggests a different underlying mechanism.

In LSMO/Alq$_3$/Al devices only one electrode is FM, and thus the spin-valve MR effect at low H is absent, the negative HFMR is still present, as shown in Fig. 2(a). The overall MR of the device closely resembles the in-plane HFMR of the LSMO film itself [Fig. 1(a)]. However, the organic diode resistance is approximately 3 orders of magnitude larger than that of the LSMO film. This implies that charge transport *across* the layers, rather than the serial resistance of the LSMO film, dictates the diode resistance, and consequently the HFMR. A similar HFMR characteristic was found at other temperatures [Fig. 2(a) inset].

Essentially the same HFMR was also obtained in diode structures made with other π-conjugated OSEC active layers such as PFO polymer and NPD small molecules [Fig. 2(b)]. These OSEC layers differ from Alq$_3$ in their band gaps, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels relative to the LSMO Fermi level, and molecular structures that all affect the device resistance. However, the MR effect of the LSMO-based devices is apparently independent of the π-conjugated OSEC spacer properties.

The similarity between the HFMR of the LSMO film and the LSMO-based organic diodes reveals that the field effect originates from LSMO, but not through its serial resistance that is negligibly small compared to the diode resistance. No HFMR was found in organic diodes with other FM than LSMO (e.g., Co or Fe). This further highlights that a common underlying mechanism of the HFMR effect in LSMO-based diodes lies in the unique properties of the LSMO film. In the metallic FM regime of Sr doping (e.g., Sr ~ 0.33), the MR effect at $T \ll T_c$ is generally believed to be caused by the suppression of the spin fluctuations upon the application of H. This, in turn, leads to a reduced electron scattering rate, and thus a smaller film resistance [7,8]. However, in LSMO-OSEC/metal structures the LSMO electrode affects the device resistance mainly through carrier injection that proceeds by tunneling and thermo-ionic emission [9,10], giving rise to a much larger resistance. Therefore, the scattering rate reduction in LSMO responsible for its own HFMR should be of little consequence to the injection process.

Carrier injection across a metal/OSEC interface is determined by the interfacial barrier height and density of states (DOS) at the metal Fermi level, E_F [9,10]. However, since the interface resistance depends exponentially on barrier height but only linearly on the metallic DOS at E_F, then the former should dominate both the injection and the HFMR. As predicted theoretically [4] and also studied experimentally [11], the shift of E_F in double-exchange FM metals can be extraordinarily large, which is an effect of the double-exchange and the dynamic Jahn-Teller mechanism on the e_g electron bandwidth [12].

In ITO/Alq$_3$/Al control devices, we did not found any significant HFMR in the small bias voltage range (< 1 V). Hence, we assume that the applied magnetic field does not significantly affect the HOMO and LUMO levels and carrier mobility in the OSEC layer, and attribute the observed HFMR in the LSMO-based devices to the LSMO-OSEC interfaces. In the bias voltage regime where "injection limited current" dominates the organic diode I-V response, the metal/OSEC interfaces determine the device resistance [9,10], but here only the LSMO-OSEC interface is relevant to HFMR. At the present time we do not attempt to fit the actual diode I-V curves, but rather analyze its magnetic-field dependence. In a magnetic field H, the E_F of LSMO shifts up by $\Delta\mu(H)$ due to the e_g-band broadening [4]. This is equivalent to an effective increase in the applied bias voltage V by $\Delta\mu(H)/e$, which in turn results in a current (resistance) increase (decrease). We can therefore reproduce the zero-field I-V curve simply by shifting the I-V curve at a finite field by a constant, i.e., $I(V, H) = I(V + \Delta\mu/e, H = 0)$. This was successfully achieved for an LSMO/Alq$_3$/Al device at $T = 4.2$ K between $H = 0$ and 7 T, as shown in Fig. 3(a). For this fit the effective

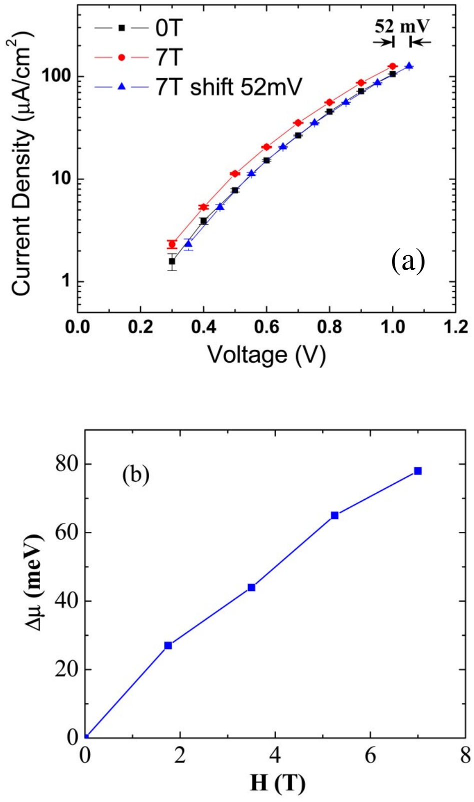

FIG. 3 (color online). (a) Current density-voltage curves of an LSMO/Alq$_3$(120 nm)/Al diode at $H = 0$ (squares) and 7 T (circles) at 4 K. The curve with triangles is obtained by shifting the 7 T curve by $\Delta\mu/e = 52$ mV. (b) The effective E_F shift, $\Delta\mu$ of LSMO vs H at 150 K.

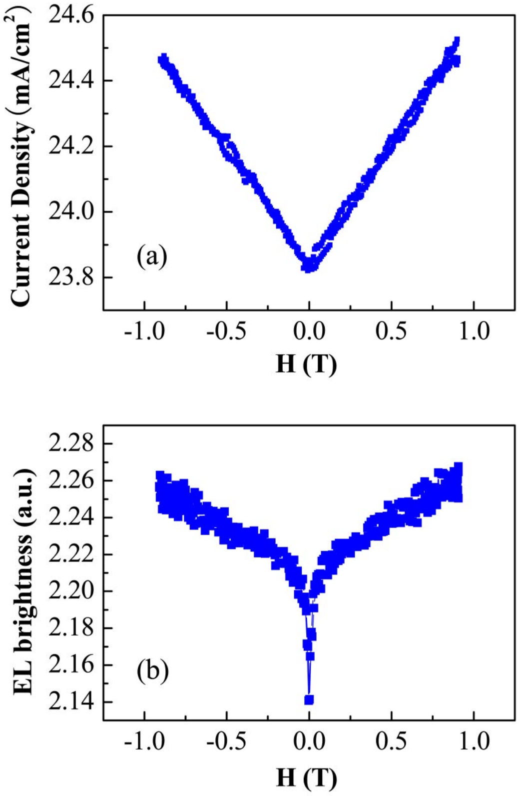

FIG. 4 (color online). (a) Current density and (b) EL intensity vs H at $V = 18$ V and 200 K for an OLED device LSMO/Alq$_3$(120 nm)/LiF/Al. The HFMR and HFMEL are in agreement with each other: $\Delta R/R \approx \Delta\mathrm{EL}/\mathrm{EL} \approx 2.5\%$.

shift, $\Delta\mu/e$, was found to be ~52 mV at 7 T, which is of the same order found in similar LSMO compounds by photoemission upon changing the temperature across T_c [11]. We have done similar analysis at $T = 150$ K, where the HFMR is at its maximum, and the obtained $\Delta\mu$ vs H dependence is shown in Fig. 3(b). The initial slope is found to be ~10 meV/T, and the magnitude agrees well with the theoretical prediction [4]. We note that this $\Delta\mu$ is about 2 orders of magnitude larger than the Zeeman energy that is the typical energy scale involved in the E_F change in a metallic system.

The field-induced injection current increase is also present at large bias voltages, where light emission in the form of EL occurs to cause the HFMEL effect. To study this effect we investigated the current and EL intensity vs H in an LSMO/NPD/Alq$_3$/LiF/Al OLED as shown in Fig. 4. As is clearly shown in Fig. 4, the HFMEL is correlated with the increase in current (or HFMR); both show a linear increase with H with a rate of ~2.5%/T. Furthermore, in OLED's fabricated using electrodes other than LSMO, such HFMR and HFMEL effects were not found. In addition to the HFMEL effect there is also a dramatic increase in the EL intensity at low fields, which is not correlated with any current increase or MR effect; its origin is not clear at the present time. However, this low-field EL increase cannot be explained by the E_F shift in LSMO, since it does appear in many OLED's with other electrodes than LSMO. As a matter of fact, the low-field MEL and MR in OLED's with nonmagnetic electrodes is a research subject of much current interest [13–17], but is beyond the focus of this work.

In summary, we have studied the HFMR and HFMEL effects in LSMO-based organic diodes and OLED's and have shown that these effects originate from the field-dependent carrier injection at the LSMO-OSEC interface caused by an anomalous E_F shift in LSMO. Owing to the uniqueness and ease of OSEC device fabrication, which does not need lattice constant matching, FM/OSEC hybrid structures may be readily used to study field effects on the electronic structures of other exotic FM materials.

We thank E. Mischenko and D. Mattis for helpful discussions. This work was supported in part by ONR/DARPA, Grant No. N00014-02-1-0595, NSFC Grant No. 50421201, and DOE Grants No. FG-02-ER46109 and No. DE-FR-04-ER46161.

---

[1] Z. H. Xiong, D. Wu, Z. V. Vardeny, and J. Shi, Nature (London) **427**, 821 (2004).

[2] K. S. Takahashi, A. Sawa, Y. Ishii, H. Akoh, M. Kawasaki, and Y.Tokura, Phys. Rev. B **67**, 094413 (2003).

[3] V. Dediu, M. Murgia, F. C. Matacotta, C. Taliani, and S. Barbanera, Solid State Commun. **122**, 181 (2002).

[4] N. Furukawa, J. Phys. Soc. Jpn. **66**, 2523 (1997).

[5] C. S. Xiong, Li Pi, Y. H. Xiong, Y. B. Jia, G. E. Zhou, Z. P. Jian, and X. G. Li, Solid State Commun. **114**, 341 (2000).

[6] We found no apparent degradation in either the spin-valve or HFMR effect in devices with reused LSMO.

[7] R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993).

[8] H. Y. Hwang, S-W. Cheong, N. P. Ong, and B. Batlogg, Phys. Rev. Lett. **77**, 2041 (1996).

[9] P. S. Davids, I. H. Campbell, and D. L. Smith, J. Appl. Phys. **82**, 6319 (1997).

[10] J. Campbell Scott, J. Vac. Sci. Technol. A **21**, 521 (2003).

[11] K. Schulte, M. A. James, L. H. Tjeng, P. G. Steeneken, G. A. Sawatzky, R. Suryanarayanan, G. Dhalenne, and A. Revcolevschi, Phys. Rev. B **64**, 134428 (2001).

[12] A. J. Millis, B. I. Shraiman, and R. Mueller, Phys. Rev. Lett. **77**, 175 (1996).

[13] T. L. Francis, O. Mermer, G. Veeraghavan, and M. Wohlgenannt, New J. Phys. **6**, 185 (2004); O. Mermer, G. Veeraghavan, T. L. Francis, and M. Wohlgenannt, Solid State Commun. **134**, 631 (2005).

[14] E. Arisi, I. Bergenti, V. Dediu, M. A. Loi, M. Muccini, M. Murgia, G. Ruani, C. Taliani, and R. Zamboni, J. Appl. Phys. **93**, 7682 (2003).

[15] G. Salis, S. F. Alvarado, M. Tschudy, T. Brunschwiler, and R. Allenspach, Phys. Rev. B **70**, 085203 (2004).

[16] J. Kalinowski, M. Cocchi, D. Virgili, V. Fattori, and P. Di Marco, Phys. Rev. B **70**, 205303 (2004).

[17] A. H. Davis and K. Bussmann, J. Vac. Sci. Technol. A **22**, 1885 (2004).