Room-temperature spintronic effects in Alq$_3$-based hybrid devices

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We report on efficient spin polarized injection and transport in long (10$^2$ nm) channels of Alq$_3$ organic semiconductor. We employ vertical spin valve devices with a direct interface between the bottom manganite electrode and Alq$_3$, while the top-electrode geometry consists of an insulating tunnel barrier placed between the “soft” organic semiconductor and the top Co electrode. This solution reduces the ubiquitous problem of the so-called ill-defined layer caused by metal penetration, which extends into the organic layer up to distances of about 50–100 nm and prevents the realization of devices with well-defined geometry. For our devices the thickness is defined with an accuracy of about 2.5 nm, which is near the Alq$_3$ molecular size. We demonstrate efficient spin injection at both interfaces in devices with 100- and 200-nm-thick channels. We solve one of the most controversial problems of organic spintronics: the temperature limitations for spin transport in Alq$_3$-based devices. We clarify this issue by achieving room-temperature spin valve operation through the improvement of spin injection properties of both ferromagnetic/Alq$_3$ interfaces. In addition, we discuss the nature of the inverse sign of the spin valve effect in such devices proposing a mechanism for spin transport.

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I. INTRODUCTION

Spin-dependent transport has been the object of intense research since the demonstration of magnetoresistive effects in metallic multilayers and magnetic tunnel junctions.$^{1,2}$ The field has evolved to the extent that commercial applications for magnetic recording and electronic memory are now available. However, achieving coherent spin transport over distances on the nanometer scale has proved difficult in normal metals and semiconductors.$^3$ This difficulty has motivated a search for new materials in which both efficient spin injection and transport can be realized. Among others, $\pi$-conjugated organic semiconductors (OSSs) have emerged as major candidates, mainly thanks to their low spin-orbit interactions and their ability to be integrated in hybrid organic-inorganic devices.$^{4–6}$

Spin injection into organic semiconductors was first demonstrated in lateral devices with highly spin polarized manganite La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) electrodes and sexithiophene (T6) as the channel material, in which room-temperature magnetoresistance (MR) has been detected.$^7$ Subsequently, a spin-valve effect in vertical devices with LSMO and cobalt electrodes was observed using tris(8-hydroxyquinoline) aluminum (Alq$_3$) as the spin transport layer (150–200 nm thick).$^8$ In the latter the spin-valve effect has shown an inverse sign, indicating a higher resistivity when the magnetizations of the electrodes are oriented parallel to each other, contrary to the standard spin-valve effect.$^{2,3}$ This behavior was later confirmed in a variety of similar devices involving the simultaneous use of LSMO and Co as spin-polarized injectors.$^9–11$ While still puzzling, this is currently one of the most well-established results in organic spintronics.

Another important parameter of the Alq$_3$-based spintronic devices which is under debate is their possible operational temperature limitation. In the literature, experimental data indicate that the highest temperature for spin injection into Alq$_3$ is close to 250 K,$^{11}$ well below the requirement for real practical applications, where room-temperature operation is mandatory. It was also speculated that the LSMO-Alq$_3$-based devices have intrinsic limitations preventing room-temperature operation.$^{12}$ On the other hand, room-temperature MR has recently been reported for devices based on magnetic tunneling, in which Alq$_3$ was used as ultrathin tunneling layer.$^{13}$

In this paper we present room-temperature spin injection and transport in an Alq$_3$-based vertical spin valve (SV) with the structure La$_{0.7}$Sr$_{0.3}$MnO$_3$ /Alq$_3$ /tunnel barrier/Co. We report on the engineering of interfaces using artificial tunnel barriers aimed at improving the efficiency of the spin injection in organic semiconductors, which guarantees a sharp definition of the organic layer thickness. We confirm the inverse spin-valve effect also for these modified geometry devices (no direct Co/Alq$_3$ interface) and propose a phenomenological explanation for it.

II. EXPERIMENT

La$_{0.7}$Sr$_{0.3}$MnO$_3$ films, 15–20 nm thick and with a Curie temperature of 325–330 K, were grown by pulsed plasma deposition (PPD) on matching perovskite substrates (NdGaO$_3$). This method, also called channel spark ablation, has been extensively used for the growth of various oxide films.$^{14,15}$ Alq$_3$ films (100–300 nm) were deposited at room temperature by organic molecular beam deposition in UHV conditions ($10^{-9}$–$10^{-10}$ mbar) on LSMO thin layers. Prior to deposition the LSMO surface was reconstructed following the annealing procedures established by photoemission spectroscopy (PES) investigations.$^{16}$ Room-temperature depo-
on provides morphologically stable amorphous organic films\textsuperscript{17,18} with molecularly flat surfaces (about 1-nm roughness). Previously we have detected spin-valve effects in devices with Alq\textsubscript{3} deposited at higher substrate temperature of 150 °C. In that case layers of about 100–200 nm thick were characterized by a roughness of around 10 nm\textsuperscript{19,20}

The Alq\textsubscript{3} layer is followed by 2-nm-thick Al\textsubscript{2}O\textsubscript{3} or LiF tunnel barriers grown by PPD and molecular beam epitaxy, respectively. The choice of Al\textsubscript{2}O\textsubscript{3} was based on its well-known properties as a tunnel barrier in magnetic tunnel junctions, while LiF barriers are extensively used in Alq\textsubscript{3}-based organic light-emitting diodes. The top Co electrode (35 nm thick) was deposited by rf sputtering.

**III. RESULTS AND DISCUSSION**

Manganite films have been characterized exhaustively in order to ensure optimal device performance. In particular, special attention has been devoted to the surface magnetic properties, which are critical for the successful use of LSMO as spin injector. Although this characterization may seem routine, it is far from trivial as surface magnetization (SM) (spin polarization) should not be taken for granted even if bulk magnetic properties are excellent. Moreover, in spite of their importance, surface properties are rarely cited when dealing with manganite complex devices. In previous works we extensively examined the potential use of manganite as spin injecting contact in connection with organic semiconductors\textsuperscript{21,22}. In particular, the LSMO postdeposition treatments have been optimized in order to recover optimal electrical and magnetic surface properties. Surface metallicity and strong circular magnetic dichroism (surface magnetization) up to room temperature were detected by PES (Ref. 21) and x-ray magnetic circular dichroism (XMCD) [Fig. 1(a)]. Magneto-optical Kerr effect (MOKE) allows us to ensure that bulk (few nanometer scale for LSMO) magnetic properties are in accordance with those published in literature [Fig. 1(b)].

We worked on the improvement of the top interface (Alq\textsubscript{3}/Co) by introducing an inorganic tunnel barrier covering the organic semiconductor. The Alq\textsubscript{3}/cobalt interface suffers from intrinsic limitations due to the direct deposition of the metal on top of a soft material, causing the diffusion and penetration of metal atoms in the organic layer, and a possible reaction with the organic molecules.\textsuperscript{8} The presence of a disordered interfacial layer is preventing both efficient and especially reproducible spin injection intensity and is probably also responsible for the extremely high switching fields (100–300 mT) presented in literature.\textsuperscript{10,23} As an example, the so-called “ill-defined layers” up to 100 nm thickness\textsuperscript{8,11} are routinely present in literature and indicate the thickness below which the material of the top electrode penetrates in the organic layer and reaches the bottom electrode providing short circuit regime. In such a situation, a systematic Alq\textsubscript{3} thickness dependence of the transport properties of vertical spin valves is hardly attainable.\textsuperscript{24}

The introduction of a thin Al\textsubscript{2}O\textsubscript{3} barrier (1–2 nm thick) between Alq\textsubscript{3} and Co results in a sharp definition of the metal/organic interface. X-ray resonant reflectivity measurements of Co film grown on top of Alq\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} are presented in Fig. 2(a). Spectra were collected on the circular polarization beam line (ELETTRA) equipped with the IRMA reflectometer at an incident photon energy of \( E = 777 \) eV. The spectra show interference fringes, indicating a well-defined multilayered structure with sharp interfaces. A fitting procedure based on the IMD code\textsuperscript{25} involving a graded interface indicated an intermixing region at the interface between OS and Co as narrow as 2–3 nm. The barrier strongly limits the penetration of the Co atoms into the organic underlayer. The intermixing value we obtained is close to the intrinsic roughness of the interface, since the molecular size is close to 1 nm (full data analysis will be presented elsewhere). On similar devices without tunnel barrier, a cobalt penetration into the Alq\textsubscript{3} of up to 25 nm has been observed.\textsuperscript{24} A typical magnetic hysteresis loop for the standard Co electrode grown on top of the Al\textsubscript{2}O\textsubscript{3} layer measured by MOKE technique (\( \lambda = 632.8 \) nm) is shown in Fig. 2(b).
Once the critical interfacial quality has been assured, we can now turn to the electrical properties of the devices. We believe that the structural improvements explained above are crucial to the enhanced device performance.

Electrical measurements of the devices ($1 \times 1$ mm$^2$) were done in a cross-bar structure using two contacts for the bias voltage and two for the measured current. Samples were inserted in a helium exchange gas cryostat placed between the poles of a magnetic field for the temperature-dependent electrical measurements. Current ($I$)-voltage ($V$) characterizations of LSVO/Alq$_3$/Al$_2$O$_3$/Co devices were strongly nonlinear, indicating tunneling injection into organic electronic states. Low-voltage resistances in the range of 1 to 10 kΩ were found for our devices, in agreement with sample geometry and organic layer thicknesses. Light-emitting effects in Alq$_3$ layers have been previously presented by us for both LSVO and Co electrodes.

Under the application of a magnetic field, the spin-valve effect was detected routinely in LSVO/Alq$_3$/Al$_2$O$_3$/Co samples (Fig. 3). In all cases, the effect had an inverse sign, with the low-resistance state corresponding to antiparallel configuration of the two electrodes and persisted for applied voltages up to 1 V. The voltage dependence of the MR effect for this kind of devices is slightly asymmetric, and it is quite similar to what we found previously in rough Alq$_3$ SVs (Ref. 19). While a more detailed investigation of the thickness dependence has yet to be performed, the MR was found to decrease with increasing organic thickness (Fig. 3 inset) as it is expected for spin/charge injection into the conducting (narrow) band of the organic semiconductor and subsequent hopping toward the opposite electrode. The further reduction in the thickness of the organic layer must be accompanied by a corresponding reduction in the lateral size of the devices. With the current size, the contribution of the electrodes to the total resistance of the device is high, and therefore a thinner device would have a resistance too low to be measured reliably.

Low-temperature MR values in excess of 10% were routinely obtained on numerous devices with a 100-nm-thick Alq$_3$ layer (Fig. 3). Higher MR values presented by other authors are probably caused by a lower effective thickness of the organic layer compared to the nominal one due to the so-called ill-defined layer.

In addition to a much better definition of the geometry, we remarkably achieved room-temperature operation of Alq$_3$-based devices as shown in Fig. 3(c). While the absolute values are still small and should be substantially improved, this provides a considerable breakthrough for the potential Alq$_3$ application in the field of spintronics.

The inverse spin-valve effect was also obtained in LSVO/Alq$_3$/LiF/Co structures, indicating that negative MR is a general feature of LSVO/Alq$_3$/Co devices rather than just an interface effect. However, MR values for LiF were much smaller than for the Al$_2$O$_3$ case (not larger than 2%) and quickly decreasing with temperature. The reasons for such behavior are not completely clear. Nevertheless it has to be mentioned that due to chemical interactions with Alq$_3$ (Ref. 29), LiF, differently from Al$_2$O$_3$, is not expected to form a well-defined buffer layer. This could worsen the quality of the Co top electrode.

We should point out that the spin injection and transport in organic spin valves are radically different from those in inorganic semiconductors. This difference perhaps also holds for the conductivity mismatch problem while this aspect has yet to be investigated deeper. Indeed, many groups succeeded in injecting a spin polarized current across a direct OS/metal interface. In the organic devices the two spin-polarized reservoirs (two external electrodes) are connected by a very narrow hopping channel at either the lowest unoccupied molecular orbital (LUMO) or highest occupied molecular orbital (HOMO) states, depending on interface energetics and intrinsic organic properties. Previously we have shown that at the LSVO/Alq$_3$ interface, a 1.1-eV barrier to the LUMO level is built while the HOMO level is separated by 1.7 eV. In addition, electronic transport in this material has a mobility two orders of magnitude higher than the hole one, a property well known and widely used in OLED applications. Thus, we can consider LUMO channel responsible for nearly 100% of the charge and spin transport in our devices. The LUMO channel is not represented by a real conducting band but rather by a pseudolocalized broadened level of 0.1-eV width, which broadens in a Gaussian way with a standard deviation $\sigma \sim 0.35$ eV at the interface. In our spin valves we first have a tunneling injection of the electrons from the LSVO into the LUMO states of Alq$_3$. This is followed by hopping conductivity across the “thick”...
Al2O3 Co

We shall discuss now the negative spin-valve effect in these and similar devices presented in literature. The existing explanation for the inverse spin-valve effect takes into account the negative (spin-down) polarization of the d electrons in Co and opposite (spin-up) polarization of the LSMO electrons.\textsuperscript{8,10} While correct as far as LSMO is concerned,\textsuperscript{42}

FIG. 5. Energy diagram for a La0.7Sr0.3MnO3/Alq3/tunnel barrier/Co organic spin valve at \( \Delta E = 0 \) V. Upper panel: Injection of spin-up electrons from LSMO into Alq3 and the alignment of LUMO with the Co spin-down band. Lower panel: Injection of spin-up electrons from Co through the Al2O3 barrier into Alq3 and the alignment of LUMO with the LSMO spin-down band. The light gray represents the spin-up bands, while the dark gray represents the spin-down ones.

Our results on the temperature dependence of MR are in agreement with the previous claim that the temperature dependence of MR in Alq3 spintronic devices is governed by manganite electrode.\textsuperscript{39} While correct in our opinion, this conclusion was not demonstrated by a straightforward data trend. Moreover the authors anticipated that room-temperature spin valve is not achievable by using the LSMO-Alq3 combination. This conclusion was based on the fitting of MR as a function of temperature with a different surface magnetization curve.\textsuperscript{39} The authors used the so-called polarized charge-carrier density (PCCD) (dashed curve in Fig. 4). This quantity consists of the convolution of SM and the density of states at the Fermi energy and decreases with temperature much quicker than that of SM alone. Attempts were made by the same group to circumvent the LSMO limitation and to achieve room-temperature operation for the Alq3-based spin valves by replacing the LSMO electrode with a Fe one, which has a much higher Curie temperature.\textsuperscript{39} Since this approach failed (the temperature behavior was even worse than for the LSMO case), the question of temperature limitations for spin injection in Alq3 remained open.

A possible improvement on the room-temperature operation efficiency can still be achieved by the enhancement of the room-temperature surface magnetization in manganese whose nanoscale distribution is still under debate.\textsuperscript{40,41} The replacement of the manganese electrode by materials with a higher Curie temperature requires, on the other hand, considerable efforts on the interface engineering in order to achieve efficient and reproducible spin injection intensity.

The dependence of the MR with temperature (Fig. 4) is helping us to identify the critical contributions to spin transport. In Fig. 4 we can observe the normalized MR versus temperature for four independent devices with a 100-nm-thick Alq3 layer and an Al2O3 barrier. The MR data are presented in square-root scale (inset) where data linearization is achieved. First, it is important to note the excellent reproducibility between the four devices. A most remarkable characteristic then is the extrapolation of data to exactly zero at the Curie temperature of the manganite, i.e., at 325 K. This allows us to draw an important conclusion—the spin transport in Alq3 and, consequently, the spin-scattering effects are temperature independent for the investigated range of temperature. This information is extremely important for the understanding of the basic rules describing the behavior of the electrically driven spin in organic semiconductors. Figure 4 shows that our data agree very well with the SM curve for LSMO of Park et al.\textsuperscript{37} The SM represents the magnetization from the top 5 Å in a standard LSMO film, as determined by spin-polarized photoemission spectroscopy\textsuperscript{37} and it is effectively the parameter of interest for device behavior.\textsuperscript{38}

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![FIG. 4. (Color online) Comparison between spin-valve magnetoresistance (MR, dots), the La0.7Sr0.3MnO3 surface magnetization (SM, solid line), and the polarized charge-carrier density (PCCD, dotted line) data from Ref. 37. Both magnitudes are plotted in reduced temperature scale normalized to the Curie temperature (\( T_C \)). The inset shows the linearized data.](image-url)
this simplified explanation does not take into account the possible effects of the Co s band, which is positively spin polarized. Moreover it has been demonstrated in a straightforward way that Co injects spin-up carriers across Al₂O₃ barrier and even across hybrid Al₂O₃/Alq₃ barriers. The sign of the MR should then be explained considering both electron currents (injected by LSMO and by Co) as spin-up currents.

While this looks apparently contradictory, the peculiar energy diagram of the full LSMO/Alq₃/Al₂O₃/Co device allows us to propose a simple phenomenological model explaining the inverse spin-valve effect (see Fig. 5). The metal/Alq₃ interfacial barriers are of about 0.5–1 eV for both interfaces.19,46 The presence of these barriers aligns the LUMO level of Alq₃ with the spin-down bands of both LSMO (Ref. 47) and Co,48,49 considering similar Fermi energy ($E_F$) values for Co and LSMO ($E_F = 4.9–5$ eV). Thus the spin-up electrons injected by either the LSMO (negative voltage) or the Co electrode (positive voltage), propagate by a hopping mechanism along the organic material where they gradually lose part of their spin polarization. Eventually, the electrons tunnel from the LUMO of Alq₃ into the spin-down bands of either the Co or LSMO electrode, respectively.

While qualitatively correct and able to justify the inversion of the spin-valve effect, the model requires operating voltages higher than 1 V, voltages at which the spin-valve effect is very weak or even absent. We cannot thus rule out a possible involvement of deep traps or impurity levels. Detailed additional investigations should be performed in order to establish precisely the spin-conducting channels in this material.

Interestingly, three (out of four) organic materials showing inverse spin-valve effect, Alq₃, T6 (sexithiophene), as well as NPB [N′-bis-(1-naphthyl)-N, N′-diphenyl-1, 1’-biphenyl-4, 4’-diamine], have LUMO levels differing by less that 0.1 eV. In addition, the Alq₃, which is a “pure” LUMO channel conductor, shows by far the best spintronic performances. In T6 and NPB only part of the current is transported by LUMO level.

In summary, we have achieved room-temperature operation for organic spin injection devices through control and engineering of the interfaces between organics and the spin-polarized electrodes. We believe that the improvement achieved by the introduction of tunnel barriers in organic spin valves will pave the way for future development of such devices, since we have demonstrated that the organic semiconductor does not represent any limitation in performance at least up to room temperature. This achievement is in a good agreement with the recent results from Santos et al., who demonstrated that in magnetic tunnel junctions the presence of a Al₂O₃ barrier increases the spin injection efficiency at the interface.

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