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Electron and spin transport studies of gated lateral organic devices

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In view of the many, often contradictory, reports of magneto-resistance (MR) in spin valve stacks containing a layer of organic semiconductor, mostly of the small molecule variety, we have investigated interdigitated lateral structures with an organic layer deposited in the narrow gap between two ferromagnetic electrodes, which are well-suited for studying charge and spin transport in novel (high resistivity) semiconducting materials. For the channel material we used three different organic semiconductors, the small molecule tris-(8-hydroxyquinoline) aluminum (Alq3), single crystals of pentacene, and the conductive polymer poly(3-hexylthiophene) (P3HT). The channel length was 80 nm. Temperature-dependent current-voltage characteristics reveal that in all instances the current is limited by field-assisted thermionic injection over an energy barrier at the metal/organic interface. No measurable magneto-resistance was observed down to 7 K. The interface energy barrier, together with the vastly different electronic structure of metals and organics close to the Fermi level, preclude spin injection. Nonetheless, unlike the case of inorganic semiconductors, the insertion of an artificial tunnel barrier at the contact did not improve spin injection. Gate-dependent measurements exhibited short-channel effects and transistor operation with on/off ratios of 10^3, but no magneto-resistance. We suggest the observations are a consequence of the formation of bipolaron-states at increasing carrier concentration. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4770230]

INTRODUCTION

The realization of an active device that combines electric control of the source-drain current, as in a field effect transistor, with the memory effect of a spin valve, has long been a goal in spin electronics. The development of the field depends upon the existence of materials and structures that can be used as effective spin-polarized current injectors, transmitters, manipulators, and detectors. Spin-polarized current injection into a semiconductor at a contact with a ferromagnetic metal is one of the possibilities that are currently being explored, typically employing interfaces between classical group IV, III-V, or II-VI semiconductors and 3d metals.[1–3] In recent years, organic semiconductors have begun to feature in spin electronics: the weak spin-orbit and hyperfine interactions in these materials lead, in principle, to very long spin life times (often in excess of tens of microseconds) and the possibility of preserving spin coherence over distances at least comparable or longer than in metals or inorganic semiconductors, despite the relatively low mobilities.[4]

Numerous studies have utilized small organic molecules[5–10] and polymers[11] in vertical spin valve structures. These spin valves contained metallic or half-metallic ferromagnetic electrodes connected vertically via a layer of π-conjugated organic material. The magneto-resistance (MR) observed in these structures was sometimes quite large, reaching a few tens percent at low temperature and occasionally exceeding 10% at room temperature,[12] in sharp contradiction with what is normally observed in inorganic semiconductors, which typically display little effect.[1] It was proposed that spin-polarized charge carriers were injected from one ferromagnetic electrode into the organic layer, where they drifted to the collecting electrode, leading to a current-perpendicular-to-plane giant magneto-resistance (GMR) effect. However, despite the initial successes, the widely varying spin diffusion lengths that were extracted pointed to a fundamental lack of reproducibility. At the same time, Vinzelberg and coworkers showed that intermixing and pinhole formation may occur during metal deposition on top of the delicate organic layers, reducing the effective organic layer thickness in a vertical junction down to just a few nanometer.[13] In such circumstances, the mechanism of the spin-dependent transport through an organic layer is better explained in terms of spin dependent tunneling across the barrier between local metallic chains embedded in the organic layer and the ferromagnetic bottom electrode.[14] Currently, it remains unclear whether early reports of MR in hybrid organic spin valves were based on GMR or tunneling magneto-resistance (TMR). Whether or not spin injection takes place in organic semiconductors is of fundamental interest, because this is an essential requirement for performing spin manipulation within a semiconductor, as is desired for the implementation of active organic spin electronics devices.[15,16]

Studies on lateral structures avoid the side effect of pinhole formation, because no metal is evaporated on top of the organic; therefore, these structures should provide the ideal platform for studying spin injection in novel organic materials. Nonetheless, there are only a few spin transport studies performed with lateral structures with molecular polymers and oligomers; a large MR signal was found on decreasing temperature by Dediu and coworkers in sexithienyl (a pioneer material in organic field effect transistors (OFETs)) using ferromagnetic electrodes of a highly spin-polarized mixed valence manganite $La_{0.7}Sr_{0.3}MnO_3$ (LSMO), for a channel length of as much as 200 nm.[17] Later, MR up to 20% was also observed at low temperature by Ozbay *et al*. in

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the conductive polymer P3HT cast in the gap between two patterned LSMO electrodes.[18] In both cases, however, due to the device geometry having symmetric contacts, the MR could not be directly associated with the magnetization of the electrodes nor their spin polarization; therefore, the origin of this effect was not completely clear.

In this paper, we describe the fabrication and the electrical characterization of short-channel lateral transport structures where three different organic semiconducting media bridge a pair of ferromagnetic metal contacts of different coercive fields. The organic materials examined are tris(8-hydroxyquinolinato)aluminum (Alq_3), single crystals of pentacene, and poly(3-hexylthiophene) (P3HT). These materials have been the subject of research in unipolar organic electronics for at least two decades and have been chosen here to represent the classes of small molecule organic semiconductors and π-conjugated conductive polymers.[19–21] The main limitation to their use in applications is the low carrier mobility, which is, indeed, a common feature of intrinsic organic materials. Nonetheless, a gate terminal acting underneath an organic channel leads to a significant enhancement of the electrical conductivity.[20,22] Our structures have been prepared on conductive silicon substrates so that beside magnetic and electrical studies, also gate dependent measurements could be performed, as in OFETs.

It turns out that there is no measureable magnetoresistance in our short-channel lateral organic spin valves, at temperatures ranging from 7 to 300 K. We discuss the nature of charge injection and transport in the organic at the contact with a metal, comparing it with the situation in inorganic semiconductors.

EXPERIMENTAL DETAILS

Experiments on spin injection from a ferromagnetic contact are typically performed using a device with simple injector–detector geometry, where two ferromagnetic electrodes are separated by a non-ferromagnetic medium. Ideally one contact is used to inject spin polarized carriers into the semiconducting material and, if the spacing between both contacts is shorter than a few spin flip lengths, the interface of the second ferromagnet would act as a spin detector, exhibiting either low or high resistance for magnetization parallel or antiparallel to the first magnet.

The devices were prepared on a heavily doped n^{++} Si wafer, which can act as gate electrode to apply a local electric field, with a 210 nm thick high-quality thermal SiO_2 oxide layer. After careful cleaning of the substrates, the silicon dioxide was chemically modified with hexamethyldisilazane (HMDS) by exposure to a saturated HMDS vapor, in order to obtain a hydrophobic surface.[23] Electron beam lithography combined with a lift-off technique was then used to define interdigitated source/drain electrodes with channel length $L = 80$ nm and alternating widths of 200 and 400 nm, to provide different coercive fields and independent magnetic switching of neighboring contacts. Electron beam evaporation was subsequently used to deposit a 2 nm thick Ti adhesion layer followed by 20 nm of $Ni_{80}Fe_{20}$ or $Co_{90}Fe_{10}$. The ferromagnetic electrodes were employed as-deposited or followed by deposition of an Al_2O_3 tunnel barrier, defined either by two-step oxidation of Al, which is intended to achieve a well-controlled oxide thickness, or by e-beam evaporation of alumina.[24] A device is shown schematically in Figure 1(a).

Finally, the organic semiconductors (Alq_3, pentacene or P3HT) were deposited on top of the patterned electrode platform. Thin films of Alq_3 were prepared in a high-vacuum organic deposition system, with base pressure $\sim 2 \times 10^{-9}$ Torr, by means of an effusion cell at a deposition rate of 0.1 nm/s. The Alq_3 films were deposited following *in situ* low-angle argon ion etching of the substrate (120 s at ~ 1 W/cm^2), to remove native oxide from the electrodes. Polymer films of regioregular P3HT were deposited from anhydrous-toluene solution by spin coating, in argon atmosphere, followed by annealing at 115 °C; the final thickness of the films was found to be typically around 150 nm by AFM.[25] Single crystals of pentacene were grown by the physical vapor transport (PVT) method. Zone-refined pentacene powder was heated to 275 °C (slightly below the sublimation temperature) in the hot zone of a tube furnace; single crystals spontaneously nucleated on the wall of the quartz tube at a temperature around 220 °C, after about an hour, keeping the temperature of the source zone constant under slow argon flow (about 1 scc/s). They grew as blue platelets with typical dimensions of several tens of micrometers in width and 2 to 10 μm in thickness, and were subsequently harvested and placed onto the prefabricated lateral transport structure, using a piezo-controlled nano-manipulator mounted inside the chamber of

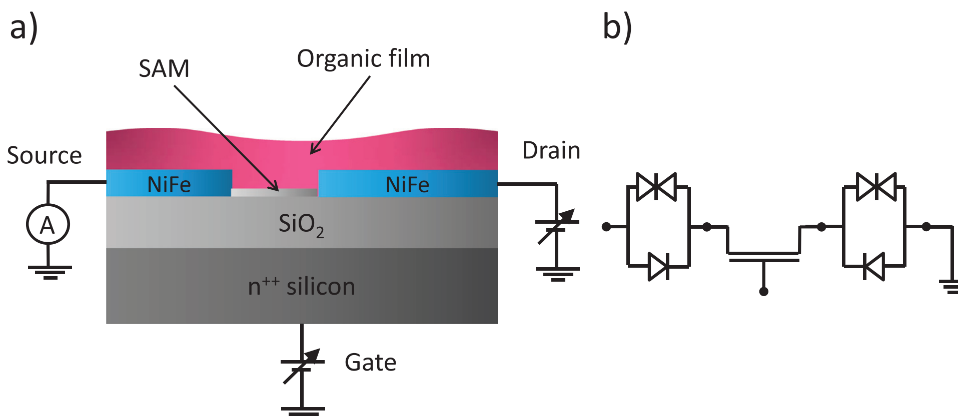

FIG. 1. (a) Schematic representation of a device used for lateral magneto-transport measurements on organic semiconductors. SAM is a self-assembled monolayer of HMDS. (b) Equivalent circuit model used to simulate the output characteristics.

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a scanning electron microscope. From SEM images, the pentacene crystals obtained by PVT appeared to have a very smooth surface. AFM investigations on the surface reveal that smooth, flat terraces are separated by monomolecular steps implying that each crystal consists of layers of pentacene sheets stacked on top of each other. The measured rms roughness on the surface of the crystal was determined to be 0.3 nm, while the measured step height of each molecular sheet is approximately 1.4 nm, resembling the length of a pentacene molecule along the main axis, known to be 1.421 nm.[26] The dimension of the *c* lattice axis resembles the molecular terraces observed by AFM, showing that the sample has single crystal properties. Elemental energy-dispersive X-ray (EDX) analysis on the crystals highlighted that the material, beyond being carbon rich, contained no heavy impurities.

The current–voltage characteristics of the devices were acquired using quantum design physical properties measuring system (PPMS) equipped with a 14 T magnet, making use of three cryogenic tri-axial leads for high impedance measurements, sub-femto-amp source-meters (Keithly 6430) and low-current pre-amplifiers. Throughout the measurements, the drain current and the gate leakage current were monitored simultaneously; so that devices with negligible leakage could be selected. Measurements were performed in high-vacuum ($p < 10^{-6}$ mbar) at temperatures ranging from 300 K to 7 K. For the MR measurements, the magnetic field was applied in the sample plane and parallel to the main axis of the electrodes.

Using similar fabrication conditions, we grew magnetic tunnel junctions with Al_2O_3 tunnel barriers as control devices, and clear TMR effects were found. This confirmed that the deposition conditions we adopted produce magnetic electrodes that have appropriate spin polarization.

RESULTS

P3HT. Initially $Ni_{80}Fe_{20}$ alloy was chosen as contact material in OFETs prepared with thin polycrystalline films of P3HT. The slow oxidation rate of nickel increases the probability of having a clean metal/organic contact interface, since the electrodes are briefly exposed to air during the fabrication process.[27] Subsequently, $Co_{90}Fe_{10}$ was also employed due to its higher electron spin polarization at the Fermi level. Examples of contacts of P3HT on Au, Co, Py, Al, and Al_2O_3/Co indicated a well-formed valence band in the organic material in this type of short-channel FET devices.[28] When P3HT and the contact metals are brought together an energy barrier rises, which, in the simplest case, is just due to the difference between the ionization potential and work function of the two materials. In fact, previous studies indicated that two other limiting factors must be taken into account in determining the Schottky barrier height, namely the reduction of the electronic surface dipole contribution to the metal work function by organic adsorbed molecules,[29] which modify the Fermi level in the metal close to the interface, due the interaction with the organic molecules which compress the metal surface states, and a large density of localized interface trap-states due to morphological disorder in the first layer of the organic that pins the Fermi level in the polymer.[28,30] Charge carrier injection into the organic can occur, in parallel, both over and through the interface energy barrier, via the mechanisms of thermionic emission, typically dominant at high temperatures, and tunneling, respectively. The devices can be modeled by using the equivalent circuit model of Fig. 1(b), to extract the barrier activation voltages for devices made with $Ni_{80}Fe_{20}$ or $Co_{90}Fe_{10}$ electrodes of 0.68 or 0.70 eV. Such values, larger than the simple rigid band offset, are consistent with the presence of mechanisms that shift the Fermi level away from charge neutrality, as outlined above.

The bottom-gate geometry employed in our device enables the investigation of charge transport in an applied electric field. In Figure 2 we show the output characteristics of a $Co_{90}Fe_{10}$/P3HT device at low temperature at different applied gate biases, from 0 to −50 V. The observed response to a local electric field exhibits the general aspects of a hole-transporting system, in which the drain current is enhanced by negative gate bias. The application of positive gate bias completely shuts down conduction in the channel. The devices exhibit short-channel effects similar to those observed in OFETs, not displaying saturation for the gate voltages typically tested (up to −100 V).[31,32] No major hysteresis in either the output or transfer characteristics was detected and the effect of the gate on the drain current is quite pronounced, with on/off current ratios of up to 10^3 at maximum source-drain bias.[28] Figure 3 illustrates the leakage current (through the source-gate circuit), as a function of source-drain voltage, for two different devices: one that is functioning correctly and one with significant leakage, we associate with defects in the oxide insulation, which have been propagated during device processing (cleaving). The gate current was constantly monitored and acquired during our measurements so as to discard any faulty device (with $I_g > 10$ pA).

To gain insight into the transport mechanisms within the organic media, we have measured the electrical characteristics on lowering the temperature when different gate voltages were applied, and estimated the resistance of the channel from the current-voltage characteristics, using the equivalent circuit model of Figure 1(b) to simulate the curves.[33] At gate

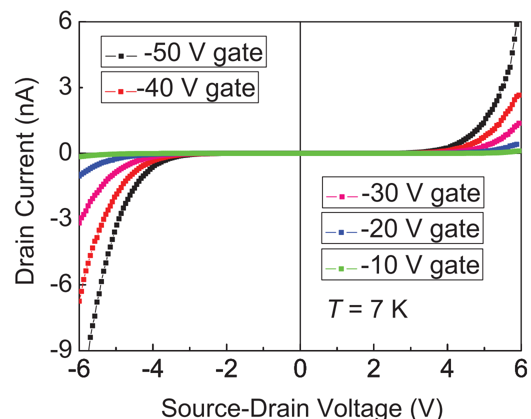

FIG. 2. Current-voltage characteristics measured at different gate biases, at constant temperature of 7 K, of a lateral transport structure prepared with $Co_{90}Fe_{10}/Al_2O_3$ electrodes and semiconducting spacer P3HT.

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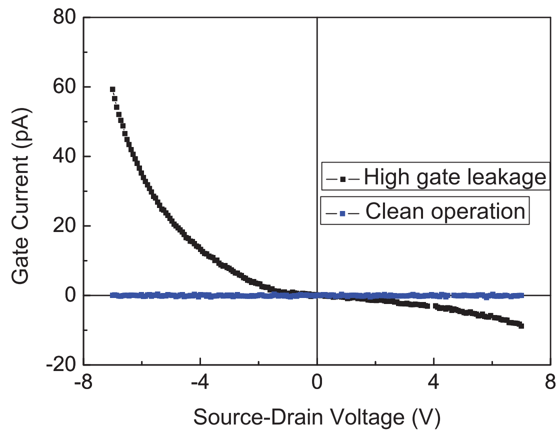

FIG. 3. Leakage current (through the source-gate circuit) as a function of source-drain voltage, for two different devices: one that is functioning correctly (in blue) and one with significant leakage (black). The diode-like curve indicates that the conductive substrate is in electric contact with the organic semiconductor; we associate this with defects in the oxide insulation that have been propagated during the device processing.

bias of −50 V, the resistance of the organic spacer is weakly dependent on temperature, changing by only a factor of two for an excursion in temperature of 200 K (Figure 4). A substantially different situation occurs when smaller gate voltages, above −25 V are applied, as the channel resistance then depends strongly on temperature and increases by a factor of ∼20. These results indicate that transport of charge at low and high gate voltages occurs via different processes. For instance, due to spatial disorder in the polymer film there exists a distribution of states situated in the gap, these states are the first to be occupied as charges are introduced, locating the Fermi level initially within the gap itself. When a low gate voltage is applied, the conduction process is understood as being field-assisted thermionic injection followed by site-to-site thermally activated hopping of holes among gap states. At more negative gate bias, the Fermi level moves towards the energy level typical of the mobility edge in the material, and is pinned there. At this energy the number of states is sufficiently high, so that electrons no longer have to be thermally activated in order to move, but they can tunnel from one centre to another by quantum mechanical hopping.[34]

In order to understand whether a spin polarized current can be injected and detected into P3HT from ferromagnetic metals the resistance has been measured at increasing temperatures starting at 7 K as a function of magnetic field up to 1 T. This is a field strength which ensures the reversal of the magnetization in the electrodes. The field was applied along the main electrode axis and scanned from 0 to −1 T, slowly reversed to +1 T along the same direction, and then brought back to zero. Gate voltage was also applied above the transistor turn-on voltage, to increase the current signal. Both negative and positive source-drain bias were tested. However, no clear spin-valve effect was observed, with either $Ni_{80}Fe_{20}$ or $Co_{50}Fe_{50}$ contacts. Any magnetoresistance effect is less than one part in 10^3.

The lack of MR in our $Ni_{80}Fe_{20}$ and $Co_{50}Fe_{50}$/P3HT spin valves is reminiscent of the situation at a ferromagnetic metal/inorganic semiconductor interface, where the conductivity mismatch problem, or the vastly different Fermi surfaces, prevents efficient spin injection.

The difficulty of spin injection from ferromagnetic metals into inorganic semiconductors can be alleviated by introducing an injection barrier.[35] The same has been proposed for spin injection at the metal-organic interface.[36] The introduction of the barrier could promote spin injection by increasing the probability of connecting states with corresponding wave vectors on either side of the barrier. Therefore, here we tried introducing a thin Al_2O_3 barrier between $Co_{50}Fe_{50}$ ferromagnetic electrodes and the conduction channel. The presence of a thin aluminum oxide layer, beyond creating a spin-dependent tunnel barrier, should prevent the excessive oxidation of the underlying ferromagnetic metal, hence removing the issue related to spin-scattering occurring in the typically antiferromagnetic native oxide layer. Furthermore, this inert layer can decouple, from a chemical point of view, the organic material from the 3-*d* metal, preventing formation of interface states.

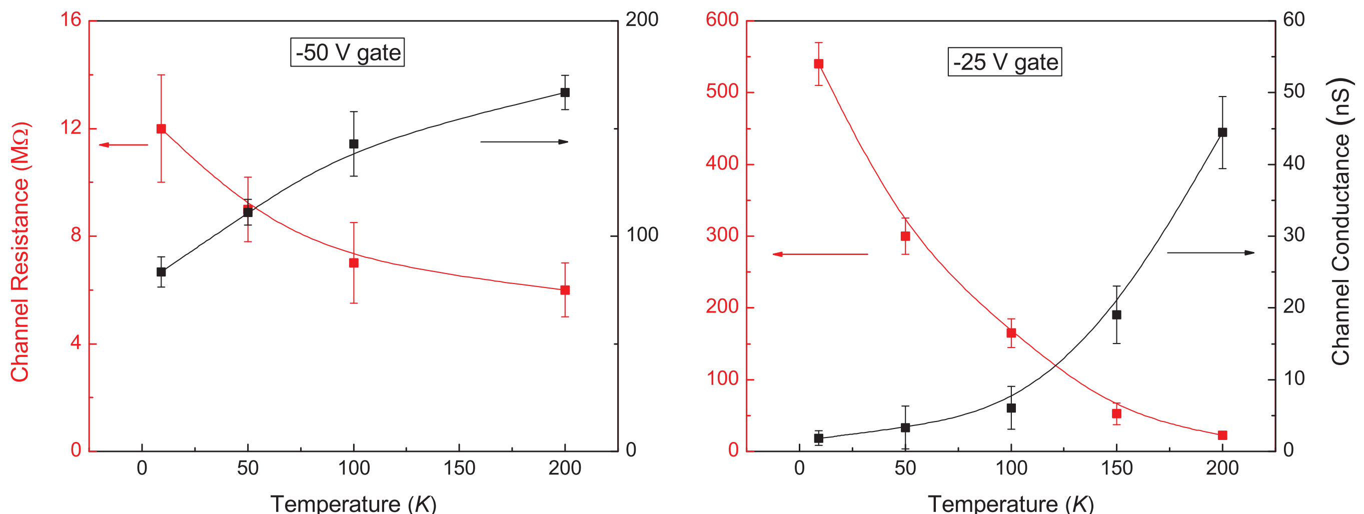

FIG. 4. Channel resistance and conductance as a function of temperature at two different gate biases of −50 V (left side of figure) and −25 V (right side), extracted from the measurements of the IV characteristics, at constant temperature, on the polymer device with $Ni_{80}Fe_{20}$ electrodes.

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The tunnel barrier was initially formed by e-beam evaporation from a source of alumina crystals to make a thin film 1.5 nm thick, briefly exposed to an oxygen plasma following deposition. No spin valve effect was observed on scanning the external magnetic field. To increase the possibilities of achieving spin injection, barriers have also been formed by natural oxidation in pure oxygen of ultra thin films of aluminum, which improves substrate coverage. Further, to fully avoid any residual oxidation of the ferromagnetic bottom layer, a device was also prepared including a 7 nm thick layer of aluminum between the electrode and the P3HT. This technique, which is less than optimal for fabricating an injection barrier, can nonetheless guarantee the protection of the ferromagnetic layer from undesired oxidation and, thanks to the reasonable spin diffusion length in Al (primarily due to its low atomic weight), should not affect, in principle, the spin polarization of the current in this thin film geometry.[24] However, no matter how we tried to perform the injection, no signs of spin injection were obtained. Since, by inserting a tunnel barrier, the interfacial impediment to spin injection is alleviated, the absence of MR indicates that some other mechanism must depolarize the spin current in P3HT. It is now important to note that injection of spin-unpolarized current from the Ti adhesion layer is not a dominant effect in our devices. The estimated screening length λ in the polymeric channels is of the order of 10 nm, therefore, the gate electric field penetrates about 50 nm (5λ) into the channel, which is well in excess of the thickness of the metal electrodes ($\sim$2 nm Ti adhesion layer, followed by 20 nm of ferromagnetic metal). Further, upon changing the top metal in the device, the source-drain conductance changes significantly—which is a clear indication that only a small fraction of the total channel current is funneled through the titanium.

The main charge carriers in organic polymers are polarons, which carry spin-1/2. Polarons are formed on the chains of the polymer in the initial stage of charge insertion; however, with increasing carrier concentration, they are known combine to form bipolarons, which are spin-0 particles.[4] Carrier mobility is very low in intrinsic organic semiconductors, and, typically, it is the application of a gate voltage which, by inducing carrier accumulation, improves the conductivity of the film. Otherwise, ion dopants may be inserted. If not, the drain currents, especially at low temperature, would be negligibly small. However, the accumulation of carriers, beyond enhancing the conductivity, may also result in the formation of bipolarons, close to the injection/detection interfaces, where carrier accumulation occurs. Because of angular momentum conservation requirements, singlet bipolarons can only form from two polarons of opposite spin. The carriers that come from the ferromagnetic electrodes, to form the accumulation layer, are, however, only partially spin-polarized. The spin polarization of most commonly used ferromagnetic metals is relatively low ($\sim$40%) and approximately constant as a function of energy around the Fermi level, up to offsets (biases) of the order of electron-volts. Within a diffusive approximation, therefore, there would be sufficient densities of polarons of either spin, within the accumulation layer, to allow for singlet bipolaron formation, only on the expense of some additional momentum scattering. This would imply that a very significant amount of spin polarization would be lost, as only a small fraction of spin-carrying polarons would be able to drift-diffuse through the accumulation layer without forming a spin-less bipolaron. In essence, the spin diffusion length would be shortened dramatically within the accumulation layer. An estimate of the carrier transit time at maximal source-drain bias and using a very modest estimate for the mobility within the channel (10^{-5} cm^2/Vs) is about 400 ns. The spin lifetime inferred from literature reports is in excess of tens of microseconds.[4] Therefore, one would normally expect (if no bipolarons are formed) that spin memory would be comfortably preserved upon transit through the channel. This was not observed. We suggest that the formation of spin-less bipolarons destroys the current spin polarization and leads to the absence of MR signal.

The validity of the above statement is unlikely to change in the complementary limit, of specular or coherent transport, close to the injection/detection interfaces. As a starting approximation the problem could be reduced to one of quantum-mechanical reflection and transmission scattering probabilities, which can be treated, in principle, using Fermi's golden rule. The process of current conversion on the ferromagnetic metal/spinless-polaronic conductor interface, in this case, should involve some enhancement of the backward-reflected waves, because of state-blocking of the final states (which would be spin-less). For states located near the Fermi level in the metal, the spin transmittivity should therefore decrease. In regimes of operation (high bias and low temperatures) where the carrier diffusion through the accumulation layer is suppressed or the layer itself is thinned down, this essentially tunneling contribution could become important. Inelastic tunneling could also contribute conduction channels that would lead to loss of spin polarization (for example, via magnon generation at the interface).

Alq3. In view of the current scientific debate around the spin injection and detection in vertical spin valve structures based on the organic material Alq_3,[7,14] we have vacuum deposited this semiconductor on a patterned lateral transport structure with ferromagnetic contacts (Figure 1(a)). The native oxide layer, formed following the lift-off, was *in situ* argon ion etched in the organic evaporation system. Despite the well-defined deposition process, the transport measurements in these short-channel devices showed poor reproducibility of their electrical properties, with a resulting low signal-to-noise ratio, as expected for conduction in insulators (Figure 5). The obtained amorphous films of Alq_3 displayed high resistivity, about $2\cdot \times 10^9$ Ω cm, from which a mobility of, at best, 10^{-5} cm^{2}V^{-1}s^{-1} can be estimated. Charge transport is injection-limited as, under applied bias, the current rises only when more than 2 V is applied between source and drain, consistent with the presence of an interface energy barrier of about 2.6 and 2.1 eV between Co and Fe, on one side, and Alq_3 on the other.[14,43] The effect of a local electric field induced by a gate voltage was almost completely masked, we believe, by charges temporarily trapped in localized states within the amorphous organic medium so that it has not been possible to discern with certainty the main carrier type. Again, no signature of magneto-resistance has been

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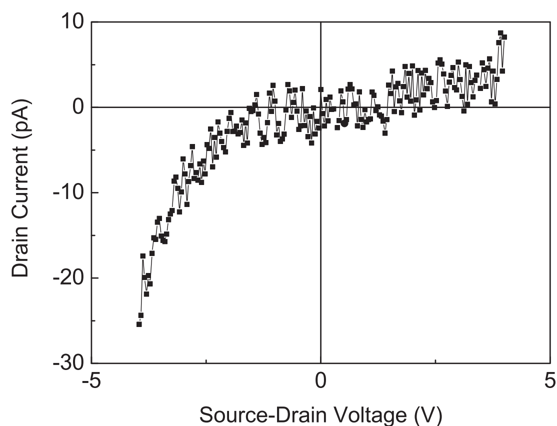

FIG. 5. Current-voltage characteristic of a device having semiconducting channel made of Alq_3, measured at room temperature with no applied gate bias.

detected, on scanning the magnetic field. The result was unchanged following the introduction of an Al_2O_3 tunnel barrier. The absence of MR in our experiments supports the tunneling interpretation of previous reports in vertical junctions, where the nominal thickness of the organic layer was similar to the electrodes gap of our devices.

Pentacene. The results on amorphous Alq_3 films triggered our interest in single crystals of pentacene. Devices have been prepared, as described in the "Experimental Details," using a pure micro-crystal to bridge two ferromagnetic $Ni_{80}Fe_{20}$ electrodes. We obtained very stable drain currents, reflecting the ordered morphology of the crystal. Figure 6 shows the current-voltage characteristics at temperatures from 7 to 300 K; the non-linear electrical characteristics indicate that injection is via field-assisted thermionic emission over an interface barrier, with an extracted activation voltage of around 1.6 V. The interface barrier at the organic-metal contact originates from the mismatch of the work function of the metal and pentacene,[37,38] along with surface adsorption[29] and the likely presence of a vacuum-gap at the contact area (due to the terraced morphology of the crystal surface). The application of a gate electrode enhanced the conductivity (Figure 7), raising the signal to

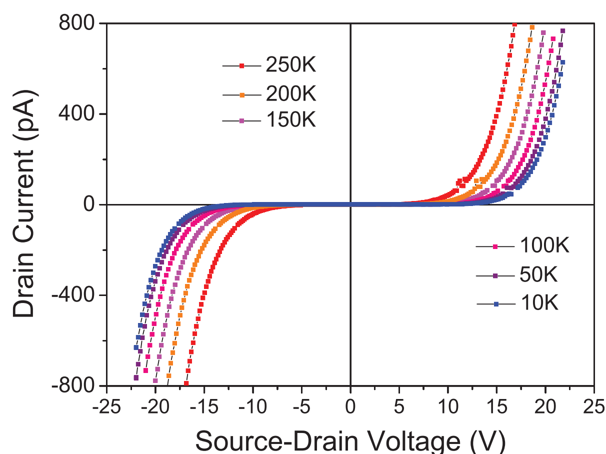

FIG. 6. Current-voltage characteristics at different temperatures for a single crystal pentacene device.

noise ratio; the effect was actually not very pronounced, with on/off ratio of about 5, presumably due to the geometry of the device in which the crystal is not in direct contact with the dielectric surface giving rise to the formation of surface electric dipoles. Nevertheless, the response to a local electric field clearly exhibited the general behavior of a hole transporting system. Resistance has also been measured as a function of magnetic field, so as to ensure independent reversal of the magnetization in the $Ni_{80}Fe_{20}$ electrodes. A set of voltages were applied at the gate and source-drain contacts that could maximize the current flowing in the device without overheating the crystal. At no temperature, between 7 and 300 K, was any significant magneto-resistance observed. The introduction of an artificial barrier of Al_2O_3, which should create a spin-dependent tunnel barrier, simply increased the energy barrier for injected carriers, without conserving the spin polarization of the carriers. This suggests that the phonon-assisted transport in oligoacene crystals does not efficiently conserve spin polarization, which is fully lost within 80 nm.[26,39]

DISCUSSION

The short-channel field effect transistors were prepared with spin-polarized electrodes and an active organic channel of poly(3-hexylthiophene), Alq_3 or pentacene in order to investigate electrical and magneto-transport in a representative group of organic semiconductors.

The devices made with the conductive polymer P3HT displayed on/off ratios up to 10^3; charge transport in the polymer appears to change from thermally assisted hopping between localized states when a low gate voltage is applied, to temperature-independent quantum mechanical hopping between states above a mobility edge for high gate biases. Low-temperature current-voltage characteristics indicate that an energy barrier builds up when the polymer and a metal are brought together, so that transport is limited by field-assisted thermionic emission above the contact barrier. Magneto-transport measurements revealed no spin-valve effect at temperatures between 7 and 300 K, which we attribute to the presence of the aforementioned barrier. In order to overcome the energy barrier, carriers are typically injected at relatively high bias, and subsequently have to thermalize. In a non-crystalline semiconductor such as P3HT this process occurs on a typical scale of 0.5 eV/ps,[40] leading to the loss of the spin polarization within a few layers of the interface.

The introduction of a thin Al_2O_3 barrier should promote spin accumulation in the non-magnetic material, as it favors injection at lower bias and should drive the carriers in the semiconductor out of local thermal equilibrium with the lattice, which normally promotes spin accumulation.[36] The artificial barrier also prevents contact chemistry and the consequent formation of in-gap interface states. However, the insertion of a tunnel barrier proved unsuccessful in terms of spin conservation in all our devices, suggesting that another intrinsic mechanism must depolarize the spin current in P3HT.

It is widely accepted that the main charge carriers in organic polymers can be either spin-$\frac{1}{2}$ polarons or spin-0

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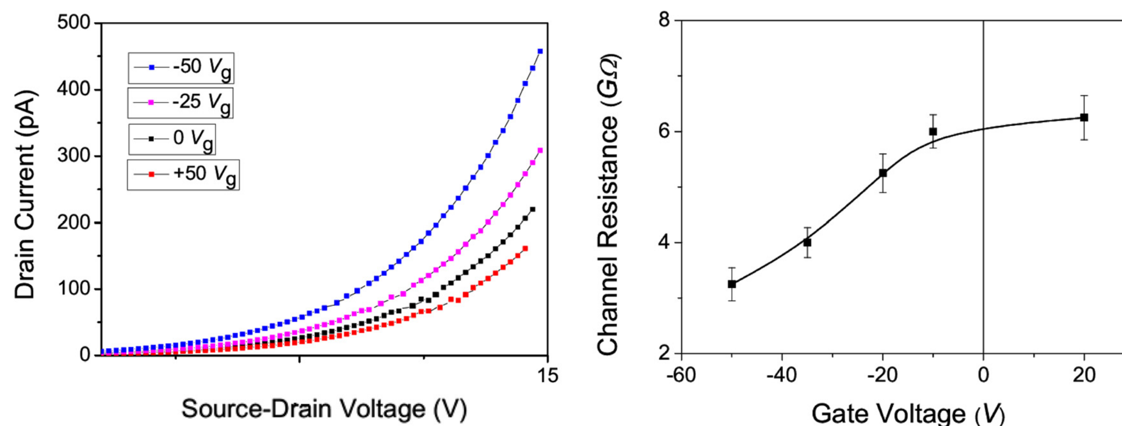

FIG. 7. Left: current-voltage characteristics at 300 K, and different gate biases, for a single crystal pentacene device. Right: channel resistance as a function of gate bias.

singlet bipolarons. Polarons are formed on the chains of the polymer when charge is first added, but at increasing carrier concentration they may combine into bipolarons; hence, the type of charge carriers changes on increasing carrier concentration, from a polaron which has spin $1/2$ to a bipolaron which has no spin.[41] In this work, due to the low carrier mobility of organic media, a gate voltage was applied to induce carrier accumulation in the organic channel. Without enhancing the conductivity in this way, the drain current would be negligibly small (i.e., there would be no signal to measure), especially at low temperatures. The accumulation of carriers, however, has the counter effect of creating bipolarons and consequently, on increasing the concentration, the spin polarization of the current will be destroyed. In order to achieve the regime of transport by quantum mechanical hopping and reasonably high signal-to-noise ratios, the above mechanism which automatically depolarizes the spin current is invoked, adding to the pre-existing impediment provided by the interface barrier.

To reduce the scattering in the bulk of the organic medium for carriers injected at relatively high bias, we chose organic single crystals of pentacene. Here, the response to a local electric field exhibited the general behavior of a hole transporting system. Magneto-transport measurements performed down to 7 K with and without applied gate voltage again showed no clear spin-valve effect. The introduction of a tunnel barrier did not enhance spin accumulation and detection, suggesting that the phonon-assisted transport, typical of oligoacene crystals, does not conserve spin orientation of carriers over distances in excess of a few tens of nanometers.

In view of the current debate on spin injection into amorphous films of Alq_3, this material has also been tested and found to be characterized by a very low mobility, at most 10^{-5} $cm^2V^{-1}s^{-1}$, and a poor signal to noise ratio, as expected for conduction in insulators. Again, no signature of magneto-resistance was observed on scanning the magnetic field to reverse the magnetization of the electrodes. This result suggests that magneto-resistance reported previously was probably tunneling magneto-resistance across short gaps, between the top and the bottom ferromagnetic contacts.[5,7,12] This interpretation is further reinforced by the presence of a high energy barrier at the contact between a metal and Alq_3 confirmed by our measurements. Under these circumstances, the application of several volts between the electrodes is necessary to achieve current injection, while in previous reports conduction was promptly achieved at low bias.

The experimental results reported in this study have revealed the obstacles towards the deployment of spin polarized electrical current in organic based electronic devices. A refinement of theoretical models explaining the mechanisms of spin injection and transport in organic semiconductors is needed, accounting for the observed presence of a Schottky barrier and the possible intrinsic depolarizing mechanisms. The synthesis of a new, more conductive, organic medium could facilitate the development of the field, but technologies based on spin will also require new methods to engineer the metal/organic interface regions, aimed in particular at reducing the interface energy barrier.

In conclusion, the lack of magneto-resistance in our organic spin valves is similar to the case of a ferromagnetic metal/inorganic semiconductor interface, where the vastly different Fermi surfaces of the two materials prevent efficient spin injection.[42] However, inserting a tunnel barrier between the magnetic electrode and the organic semiconductor did not improve spin injection.[35] This suggests possible intrinsic spin-depolarizing transport in organic conductors; we attribute this to the fact that the main type of charge carriers in the organics is the bipolaron, which carry no spin.[41] That charge carriers need to be promoted over the barrier before entering the organic layer indicates that the magneto-resistance reported previously in vertical stacks with an organic spacer, where significant conduction was achieved at low bias, is a tunneling magneto-resistance effect, rather than a manifestation of spin-polarized transport through the organic semiconductor itself.

Although they do not exhibit spin-conserved transport, the high-performance polymeric transistors achieved during this study may prove useful in other studies, which focus on the development of new organic electronic devices.

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