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Magnetoresistance in Hybrid Organic Spin Valves at the Onset of Multiple-Step Tunneling


Department of Applied Physics, cNM, Eindhoven University of Technology, The Netherlands

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By combining experiments with simple model calculations, we obtain new insight in spin transport through hybrid, CoFeB/Alq3 layer [3] and spin transport in LSMO/Alq3 (>30 nm) based devices [4,5] have been reported, thereby considerably stimulating the interest in organic spin valves [6–12]. However, spin injection and transport in an organic semiconductor are widely debated and similar results could also be interpreted within the classical tunneling concept [7,8,10]. Therefore, planar-type spin valves [4,9] and spin valves with insulating tunnel barriers [12] have been investigated to exclude tunneling transport via interdiffused clusters. Recently, direct observation of injected spin-polarized carriers inside the organic film have been reported [13,14]. Nevertheless, there still is a lack of consensus about the role of defect states [15], and little is known about the spin relaxation mechanisms.

Because of the insignificant spin-orbit spin relaxation, and since the time in between two successive hops could be relatively long (often >10 ns [16]), the electron spin on a localized molecular site can become particularly sensitive to small magnetic fields, for instance the randomly oriented localized molecular site can become particularly sensitive to a lack of consensus about the role of defect states [15], and little is known about the spin relaxation mechanisms.

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In that regime, we will show that the experimentally observed modification of the hysteretic magnetoresistance curve is in line with model calculations including spin precession in the presence of hyperfine coupling.

Before we examine the detailed magnetic field dependence of the resistance, we first introduce a basic model that describes the competition between direct and two-step tunneling to derive the characteristic change in the resistance as a function of the Alq3 thickness [Fig. 2(a)]. We consider an Alq3 layer with a thickness d, a barrier height U, and a homogeneous distribution of molecular sites with linear density N, contacted on both sides by a ferromagnetic (FM) electrode. The extinction of the wave function in the Alq3 layer is then defined as \( \kappa = 2 \sqrt{2mU/\hbar} \). d and n1 are the position and the occupation, respectively, of an intermediate site in the barrier. First, we assume only forward hopping. The direct tunneling current \( J_{\text{direct}} \) is proportional to \( \exp(-\kappa d) \). The two-step tunneling current \( J_{\text{two-step}} \) follows from current conservation at the intermediate site, \( J_{\text{01}} = J_{\text{12}} \), and subsequent solving \( n_1 \) from \( (1 - n_1) \exp(-\kappa d_1) = n_1 \exp(-\kappa(d - d_1)) \).

In Fig. 2(c) the normalized \( J_{\text{two-step}} \) has been plotted for all possible \( d_1 \). The dominant contribution to the two-step tunneling current will be, by means of self-selection, via sites halfway the barrier with \( d_1 \approx d/2 \), for which the total transmission is maximum. The total current is proportional to a weighted superposition of direct tunneling and two-step tunneling current.

Organic semiconductors hold exceptional promise for spintronics [1,2]. Spin-polarized tunneling through an ultrathin (0–4 nm) Alq3 layer [3] and spin transport in LSMO/Alq3 (>30 nm) based devices [4,5] have been reported, thereby considerably stimulating the interest in organic spin valves [6–12]. However, spin injection and transport in an organic semiconductor are widely debated and similar results could also be interpreted within the classical tunneling concept [7,8,10]. Therefore, planar-type spin valves [4,9] and spin valves with insulating tunnel barriers [12] have been investigated to exclude tunneling transport via interdiffused clusters. Recently, direct observation of injected spin-polarized carriers inside the organic film have been reported [13,14]. Nevertheless, there still is a lack of consensus about the role of defect states [15], and little is known about the spin relaxation mechanisms.

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In this Letter, we discuss how hyperfine fields can influence the spin injection and spin transport in organic semiconductors. Using a spin valve with a compound barrier, we have identified the transition regime between direct tunneling through the compound barrier and two-step tunneling via a low density of localized, intermediate (molecular or defect) states near the Fermi level. Only in the latter case hyperfine field coupling plays a significant role. In that regime, we will show that the experimentally observed modification of the hysteretic magnetoresistance.

FIG. 1 (color online). Spin precession around the sum of the hyperfine field \( \vec{H}_{hf} \) and the applied magnetic field \( \vec{H}_a \) on a molecular site, only showing downstream tunneling from or to majority and minority 3d spin bands of the FM electrodes.

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plasma oxidized. Deposited by dc magnetron sputtering and is subsequently evaporated, and the whole substrate temperature of 110 K. Finally, a Co top electrode from a Knudsen cell at a rate of...parabolic and slightly asymmetric (not shown), which suggests tunneling as transport mechanism. In Fig. 3 (open circles), the resistances of all spin valves showing magnetoresistance (yield of \( \sim 40\% \)) have been plotted as a function of \( d_{\text{Alq}} \). For \( d_{\text{Alq}} = 2-4 \) nm, the exponential increase of resistance levels off, which we assign to the predicted transition to the regime of two-step tunneling. Upon cooling to 4 K the conductance decreases to 60% of the conductance at 300 K (not shown). This generally rules out that charge transport through metallic filaments or via pinholes is dominant [7].

Subsequently, the magnetic field dependence of the spin-valve resistance has been measured for different \( d_{\text{Alq}} \). First, we will analyze the magnetoresistance (MR), defined by \( (R_{\text{ap}}/R_{\text{ap}} - 1) \times 100\% \), as a function of \( d_{\text{Alq}} \) (Fig. 3, solid squares). \( R_{\text{ap}}(\text{ap}) \) is the spin-valve resistance for (anti-)parallel magnetization alignment. Already for 1 nm, still in the regime of direct tunneling, the MR significantly reduces compared to a measured MR of 34% for a single \( Al_2O_3 \) barrier. After the onset of two-step tunneling, for \( d_{\text{Alq}} \geq 2 \) nm, the MR decreases even further. We note that none of those devices with more than 1 nm \( Al_3 \) shows a MR larger than 10%, which is in line with organic spin valves with Co, Fe, or Ni electrodes [3,11].

To obtain a quantitative interpretation of the resistance and MR as a function of \( d_{\text{Alq}} \), we extend our model. (i) We include the spin dependence of the electrons. Therefore, we replace \( n_1 \) by \( n_{\uparrow} \) and \( n_{\downarrow} \) and take into account the normalized spin occupancy in the FM electrodes \((1 ± P_0)/2 \) and \((1 ± αP_2)/2\), with \( P_0 \) and \( P_2 \) the spin polarization of the injection and detection electrode, respectively, and \( α = (−)1 \) for (anti-)parallel magnetization alignment. (ii) We add an \( Al_2O_3 \) layer with thickness \( d_{\text{Alq}} \) and barrier height \( U_{\text{Alq}} \). (iii) Because the energy penalty is modest [16], we allow double occupancy of a site by electrons with opposite spin directions. (iv) Since our aim is to solve the tunnel rates in the low bias, Ohmic regime, we permit back hopping by a rate according to the Fermi-Dirac distribution.

\[
J \sim (1 - Nd)J_{\text{direct}} + N \int_0^d J_{\text{two-step}}(d_1)dd_1. \tag{1}
\]

With increasing \( d \), two-step tunneling is favorable. Because both transmissions of the two-step tunneling process are proportional to \( \exp(−kd/2) \), the total resistance \((\sim 1/J)\) will increase exponentially with half the slope of the regime of direct tunneling [Fig. 2(d)]. Thereby, we can identify the onset of two-step tunneling.

\( Ta/CoFeB/Al_2O_3/Al_3/Co \) spin valves were fabricated completely \textit{in situ} at base pressures \(<1 \times 10^{-8} \) mbar on glass substrates via shadow masks in a cross bar configuration, defining a junction area of \( 0.3 \times 0.3 \) mm\(^2\). \( Al_2O_3 \) enhances the growth characteristics of \( Al_3 \) and improves the spin injection and detection efficiency [3]. On a \( Ta(2 \) nm)/CoFeB(2 nm) bottom electrode \( Al(1.2 \) nm) is deposited by dc magnetron sputtering and is subsequently plasma oxidized. \( Al_3 \) \( (d_{\text{Alq}} = 0-4 \) nm) is evaporated from a Knudsen cell at a rate of \( \sim 0.04 \) Å/s keeping a substrate temperature of 110 K. Finally, a Co top electrode of about 20 nm thickness is evaporated, and the whole sample is capped by 5 nm SiO\(_2\). The valence band spectra for increasing \( Al_3 \) thicknesses deposited on \( Al/Al_2O_3 \) [see Fig. 2(b)] as well as on Co (not shown) surfaces have been measured with ultraviolet photoemission spectroscopy. Results show a disappearance of the \( Al_2O_3 \) valence band between 1.0 and 1.5 nm, indicating that a closed layer of \( Al_3 \) has been obtained, although a small density of pinholes cannot be completely excluded via this technique.

To be able to identify when two-step tunneling dominates over direct tunneling, we have measured the \( I-V \) characteristics with a four-point probe technique at various temperatures and \( d_{\text{Alq}} \). All \( dI/dV \) are parabolic and
With these refinements, the total resistance \([\sim 1/J]\) from Eq. (1) has been calculated for reasonable parameters \((U_{Alq3} = 2.5 \text{ eV, } U_{Al2O3} = 0.4 \text{ eV, and } d_{Alq3} = 1 \text{ nm})\) [3], and is subsequently fitted to the experimental results (Fig. 3 solid line, using \(N = 3 \times 10^{-5} \text{ Å}^{-1}\)). Three regimes can be distinguished (Fig. 3, top axis): (I) For low \(d_{Alq3}\), direct tunneling dominates. (II) This regime is characterized by two-steps tunneling, and the transmission through the \(Alq3\) barrier is smaller than through the \(Alq3\) barrier. The largest current contribution comes from tunneling via a site near the \(Alq3\)/\(Alq3\) interface, and the resistance will hardly change with \(d_{Alq3}\). (III) For large \(d_{Alq3}\), two-step tunneling dominates and the total resistance will exponentially increase with half the slope of the first regime. Finally, for thicker organic layers the number of tunnel steps increases and the resistance will increase with an even lower slope.

Subsequently, using \(P_0 = P_2 = 0.4\), the MR has been calculated and is plotted as a function of \(d_{Alq3}\) (Fig. 3, solid line, normalized to MR \([d_{Alq3} = 0])\). In the regime of direct tunneling (I), the modeled MR is unaltered. However, for two-step tunneling (regimes II and III), the model predicts that the MR reduces at least with a factor \(\approx 4\), which matches with the maximum experimentally found MR. The factor 4 can be explained as follows. Tunneling via an intermediate site results in an intrinsic loss of MR by a factor 2 [19]. Additionally, as can be seen in Fig. 2(c), the MR is highest for sites for which transmissions through both tunnel barriers are equal, i.e., because the dominant current contribution is also via these sites, the system self-optimizes its MR. Weighting the MR for the current contribution over all intermediate sites predicts an extra averaged loss of MR by approximately a factor 2. In regime II, the transmission through both tunnel barriers cannot be equal, predicting an extra MR loss.

The even lower measured MR can possibly be explained by refining the model by (i) including a strong hybridization at the \(Alq3/Co\) interface that results in more interface sites, thereby forcing tunneling via sites with unequal transmission of both barriers (Fig. 3, dashed lines), (ii) permitting more than two tunnel steps, which may lead to a further decrease of MR, (iii) lowering of the spin polarization of Co adjacent to \(Alq3\), and (iv) including spin precession due to hyperfine coupling, thereby not reaching the maximum resistance for antiparallel magnetization alignment as explained below.

Let us now analyze in more detail the hysteretic magnetoresistance curves for devices with 1, 2, and 4 nm \(Alq3\) [Figs. 4(a)–4(c)], which are representative for the direct, the transition, and the two-step tunneling regime, respectively. The MOKE measurement in Fig. 4(d), performed on the spin valve with 4 nm \(Alq3\), displays nearly instantaneous switching of the magnetizations of both electrodes. These differences in coercivities yield parallel and antiparallel magnetization alignment, resulting in the low and

FIG. 4 (color online). Magnetic field dependencies for CoFeB/\(Alq3/Alq3\) (1, 2, 4 nm)/Co spin valves (a)–(c) measured (e)–(g) modeled. (d) Magnetization curves of the junction and bottom electrode of the sample with 4 nm \(Alq3\). (b) Representative calculation of normalized current versus \(\theta\), with indications of applicable areas for large and small \(H_{hf}\). (h) Representative calculation of normalized current versus \(\theta\), with indications of applicable areas for large and small \(H_{hf}\).
[Figs. 2(c) and 3] the spin precession frequency around the total magnetic field, \( g \frac{d}{dt} \mathbf{H}_{\text{tot}} \), is at least an order of magnitude larger than the tunnel rate \( 2\pi \exp(-\kappa d) / t_{\text{at}} \). Herein, the Landé-factor \( g = 2 \) and the attempt time \( t_{\text{at}} = 1 \) fs. Thereby, we have experimentally fulfilled the necessary precondition to use a time averaged projection operator \( \mathbf{M}_{\pm \pm} \), to describe the hopping probabilities from the precessing spinor states \( \chi_{1 \pm}(t) \), expressed in terms of spin-up and spin-down states, to the spinor states \( \chi_{2 \pm} \) in the detection electrode. Using these ingredients, we have again solved the tunnel rates like in our basic model approach. The normalized two-step tunneling current can be more generally expressed as \( 1 + \frac{A_{p} + \text{ap}}{\cos(\theta)} \), for which \( A_{p} = 0.18 \), \( A_{\text{ap}} = -0.20 \), and \( 3 \) mT has been reconstructed of the Gaussian hyperfine field distribution [Fig. 4(g)]. The magnetoresistance curves can be interpreted as follows. For \( H_{a} \gg H_{\text{hf}} \), spins preserve their alignment with the external magnetic field \( \theta = 0 \) in Fig. 4(h) and the resistance difference between parallel and antiparallel alignment is expected to be similar to the case of direct tunneling. For \( H_{a} \ll H_{\text{hf}} \), each spin at a molecular site precesses around \( H_{\text{hf}} \). Averaged over all occupied sites, these total sums of hyperfine fields will have a spherical distribution \( \theta < \theta < 2\pi \) in Fig. 4(h)]. This results in an increased (decreased) resistance for parallel (antiparallel) magnetization alignment. For \( 2 \) nm Alq3, the direct tunneling current approximately equals the two-step tunneling current as shown in Fig. 3, resulting in a weighted average of the magnetoresistance curves for \( 1 \) and \( 4 \) nm Alq3 [Fig. 4(f)].

Several features predicted by the model are present in our experimental results [e.g., Figs. 4(c) and 4(g)], like the gradual and sharp resistance change accompanying the transition to and from parallel to antiparallel magnetization alignment of the electrodes. Second, the reproducible full width half maximum of the symmetric modification corresponds to a typical value for \( H_{\text{hf}} \) [17,20].

We have several reasons why we exclude a different interpretation for the symmetric contribution. First, we exclude that the effect originates from magnetic switching of the bottom CoFeB electrode, because this would lead to identical normalized magnetoresistance curves. Second, tunneling via regions in the top Co electrode with an altered easy axis is improbable, because this would give an opposite sign of the symmetric modification for antiparallel magnetization alignment. Third, if the symmetric modification would be the result of the resistance of the electrodes, of the Alq3 barrier or of the interface, we would have observed a reduction of the symmetric contribution considering the tendency of increasing spin-valve resistance for increasing \( d_{\text{Alq3}} \) (Fig. 3). Finally, we consider it unlikely that transport via sites next to paramagnetic clusters or via sites exposed to stray fields contributes to the symmetric contribution, because one would expect in this case a wide distribution of magnetic field scales, associated with the diversity of cluster sizes and the disordered landscape of protrusions at the Alq3/Co interface.

In conclusion, by modeling the spin transport through Alq3/Alq3, we can explain the characteristic changes in the \( I-V \) behavior at the onset of multiple-step tunneling, as well as the intrinsic loss of MR. Furthermore, spin precession in the presence of hyperfine coupling has been analyzed, by which the measured magnetoresistance curves can be recovered for variable Alq3 thickness.

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