

Observation of extremely long spin relaxation times in an organic nanowire spin valve

S. PRAMANIK¹, C.-G. STEFANITA¹, S. PATIBANDLA¹, S. BANDYOPADHYAY^{1*}, K. GARRE², N. HARTH² AND M. CAHAY²

¹Department of Electrical and Computer Engineering, Virginia Commonwealth University, Richmond, Virginia 23284, USA

²Department of Electrical and Computer Engineering, University of Cincinnati, Cincinnati, Ohio 45221, USA

*e-mail: sbandy@vcu.edu

Published online: 18 March 2007; doi:10.1038/nnano.2007.64

Organic semiconductors that are π -conjugated are emerging as an important platform for 'spintronics', which purports to harness the spin degree of freedom of a charge carrier to store, process and/or communicate information¹. Here, we report the study of an organic nanowire spin valve device, 50 nm in diameter, consisting of a trilayer of ferromagnetic cobalt, an organic, Alq₃, and ferromagnetic nickel. The measured spin relaxation time in the organic is found to be exceptionally long—between a few milliseconds and a second—and it is relatively temperature independent up to 100 K. Our experimental observations strongly suggest that the primary spin relaxation mechanism in the organic is the Elliott–Yafet mode, in which the spin relaxes whenever a carrier scatters and its velocity changes.

The spin-orbit interaction in organic semiconductors is weak, which should lead to long spin relaxation times². As a result, these materials are attractive candidates for spintronics. Many organics are also optically active³, which bodes well for opto-spintronic chips, where optics and spintronics can be integrated to perform seamless signal processing and communication functions. Both thin-film organic spin valve structures¹ and molecular spin valve structures⁴ have been demonstrated, and some theoretical effort has also been made to understand spin transport in such systems^{5–8}. However, not much work has been reported for nanowire organic structures, which may become important constituents of opto-spintronic chips because of the high density with which they can be produced. Here, we report the study of nanowire organic spin valve structures, focusing on the measurement of magnetoresistance, the spin diffusion length and the spin relaxation time. These studies also shed some light on the dominant spin relaxation mechanism in the organic.

We fabricated 50-nm-diameter nanowire spin valve structures consisting of three layers: cobalt, Alq₃ (tris-(8-hydroxyquinolinolato)aluminium) and nickel. The structures were synthesized in a porous alumina membrane containing a well-ordered hexagonal close-packed arrangement of 50-nm pores⁹. A schematic is shown in Fig. 1.

Typical magnetoresistance traces of the nanowire spin valves at three different temperatures are shown in Fig. 2, where the magnetic field is parallel to the axis of the wires. There is a

background monotonic positive magnetoresistance, as is often observed in such structures^{10–12}. Superimposed on this background, we find non-monotonic magnetoresistance peaks located between fields of 800 Oe and 1,800 Oe, which are approximately the coercive fields of the nickel and cobalt layers^{9,13}. These peaks are the tell-tale signatures of the spin valve effect¹. Their heights decrease with increasing temperature and are barely visible at 100 K.

The magnetoresistance peaks could also arise from anisotropic magnetoresistance (AMR) effects in the Co and Ni contacts^{14,15}. We rule this out for a simple reason. In our structures, we have three 'resistors' in series: cobalt, Alq₃ and nickel. The organic is by far the most resistive of these three, and therefore dominates the total resistance. In fact, the resistance change associated with the peaks is three orders of magnitude larger than the total resistance of the metallic ferromagnets. Therefore, the peaks must be associated with the organic and cannot be caused by AMR effects in cobalt or nickel.

From the relative height of the spin valve peak $\Delta R/R$, we can extract the spin diffusion length in the Alq₃ layer following the technique of ref. 1. We first assume that the spin polarization at the Fermi energy of the injecting ferromagnetic contact is P_1 and that there is no loss of spin polarization at the interface between Alq₃ and the injecting contact because of the so-called 'self adjusting capability' of the organic¹⁶ invoked in ref. 1. The self-adjusting capability is a 'proximity effect' in which the region of the organic in contact with a ferromagnet becomes spin polarized up to a short distance (few lattice constants) into the organic. As a result, there is no abrupt loss of spin polarization at the interface. It turns out, however, that the measured spin diffusion length is not particularly sensitive to the spin polarization of the contacts, so that even if there were any abrupt loss of spin polarization at the interface, it would not affect our result significantly. Next, we assume, as in ref. 1, that there is a thin Schottky barrier at each organic/ferromagnet interface. Injected carriers tunnel through the first interface, which is too thin to cause spin randomization. After this tunnelling, the carriers drift and diffuse through the remainder of the organic layer, with exponentially decaying spin polarization $P_1 \exp[-(d-d_0)/\lambda_T]$, where d is the total width of the organic layer, d_0 is the total

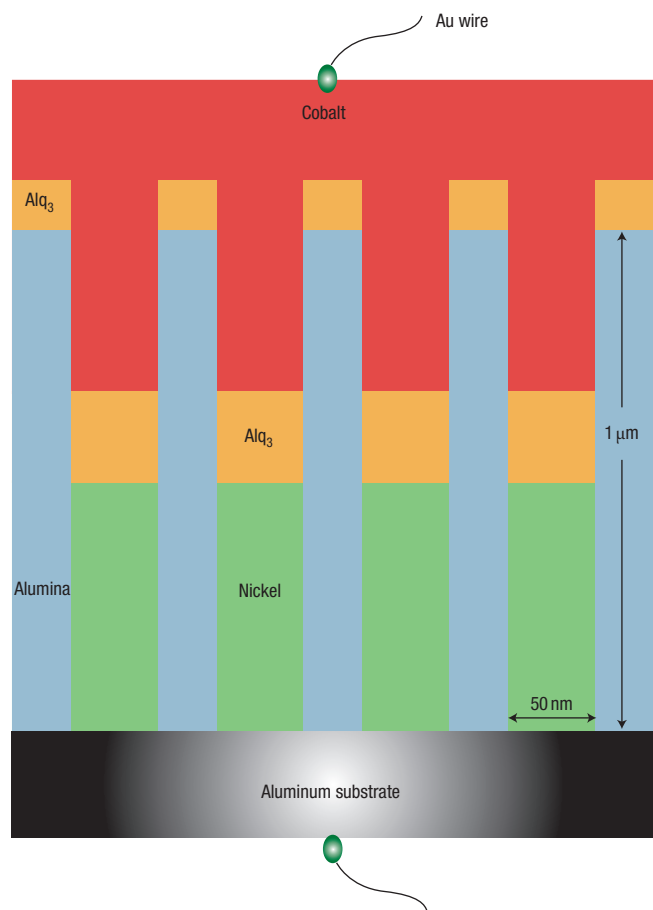


Figure 1 Schematic representation of a nanowire spin valve structure.

width of the two Schottky barriers and λ_T is the spin diffusion length in Alq_3 at a temperature T . The exponential decay follows from the drift-diffusion model of spin transport¹⁷. Finally, these carriers arrive at the detecting contact where there is a second Schottky barrier, through which they tunnel to cause the current. If the spin polarization at the Fermi level of the detecting contact is P_2 , then $\Delta R/R$ is given by the Julliere formula¹⁸

$$\frac{\Delta R}{R} = \frac{2P_1P_2e^{-(d-d_0)/\lambda_T}}{1 - P_1P_2e^{-(d-d_0)/\lambda_T}} \quad (1)$$

In our structures, $d_0 \ll d$, because $d = 33$ nm and d_0 is the width of the tunnelling barrier, which must be less than 1 nm in order to produce any measurable current in the samples. In the following, we prove that $d_0 \ll d$. In that case, the loss of spin polarization in tunnelling through the ultra-thin potential barrier is negligible. Therefore, P_1 is approximately the spin polarization of the injecting contact. As the spin polarizations in cobalt and nickel at their Fermi energies are 42% and 33%, respectively¹⁹, $P_1 = 0.42$ and $P_2 = 0.33$.

In order to determine the value of d , we have carried out transmission electron microscopy (TEM) of the nanowires. The wires were released from their alumina host by dissolution in very dilute chromic/phosphoric acid, washed, and captured on TEM grids for imaging. The TEM micrograph of a typical wire is shown in Fig. 3a. The Alq_3 layer thickness d is found to be

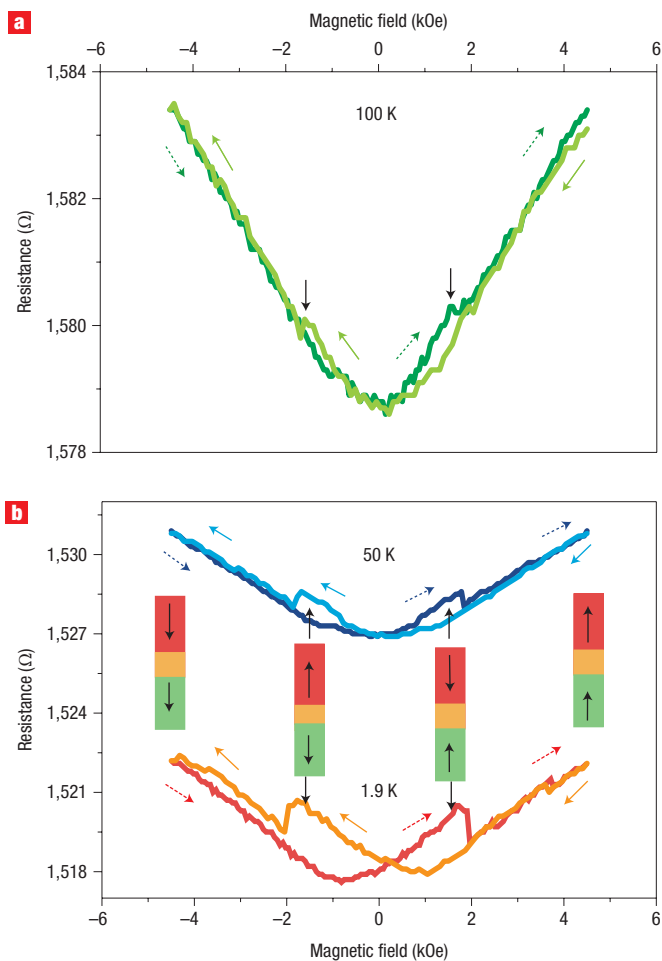


Figure 2 Magnetoresistance traces at different temperatures.

The magnetoresistance traces shown are for nanowires with a ~ 33 -nm Alq_3 layer. **a,b**, Traces with the magnetic field parallel to the axis of the wires at temperature of 100 K (**a**) and at temperatures of 1.9 K and 50 K (**b**). The coloured solid and broken arrows represent reverse and forward scans of the magnetic field, respectively. The parallel and antiparallel configurations of the ferromagnetic layers are shown within the corresponding magnetic field ranges in Fig. 2b.

33 nm, which is quite close to the layer thickness estimated during fabrication (30 nm). This agreement gives us confidence that d does not vary too much from one wire to another. We assume that it varies by ± 5 nm when we calculate λ_T from equation (1).

Current–voltage characteristics of the nanowires are shown in the inset of Fig. 3b. These characteristics are reversible with no hysteresis. They are symmetric because of equal coupling to the contacts²⁰, but are nonlinear between -3.5 and 3.5 V at all measurement temperatures, indicating that the contacts are Schottky in nature. This means there has not been significant interdiffusion of Co or Ni into the Alq_3 layer, as that would have produced an ohmic contact. As a result, the layer thickness d is well-defined in the nanowires, which allows us to apply equation (1) to estimate λ_T .

In estimating λ_T from equation (1), we assume that $d - d_0 \cong d$. If this approximation is valid, then the estimated λ_T will be independent of d . To confirm this, we fabricated another set of

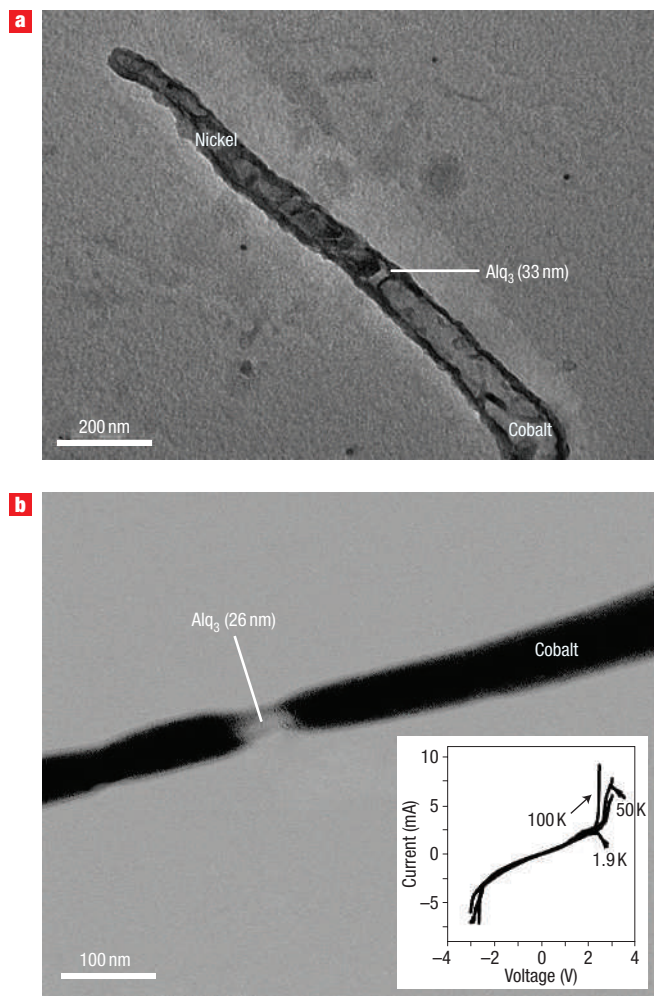


Figure 3 TEM images of typical nanowire spin valve structures. **a, b** TEM images of a typical nanowire spin valve structure from the first set (**a**), showing that the AlQ₃ layer width is about 33 nm, and the second set (**b**), showing that the AlQ₃ layer width is about 26 nm. The inset shows the measured current versus voltage characteristic at three different temperatures.

samples with slightly smaller d . Fig. 3b shows the TEM micrograph of a wire from this set where the layer thickness is found to be 26 nm. The quantity λ_T measured from this set at any temperature agrees (to within $\sim 10\%$) with that measured from the other set at the same temperature. For example, at a temperature of 50 K, the value of λ_T measured in the set with $d = 33$ nm is 4.25 ± 0.75 nm, whereas that measured in the set with $d = 26$ nm is 3.95 ± 0.75 nm. The difference between these two values is only 7.5%, which is less than the uncertainty of 19% in the measurement (accruing from the ± 5 nm uncertainty in d), supporting the conclusion that λ_T is reasonably independent of d . The values of λ_T as a function of temperature are plotted in Fig. 4a for both $d = 26$ nm and $d = 33$ nm.

Comparing the measured values of λ_T with those reported in thin films of AlQ₃ (45 nm at 4.2 K; ref. 1), we find that in a nanowire λ_T has been reduced (or equivalently, the spin relaxation rate has increased; see Supplementary Information) by almost an order of magnitude. We use this result to better understand which spin relaxation mechanism is possibly dominant in the organic AlQ₃.

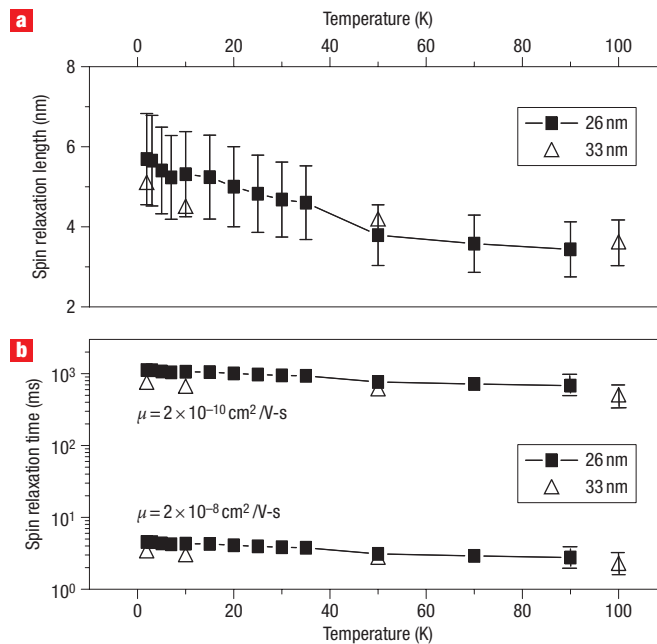


Figure 4 Temperature dependence of the spin relaxation length and time.

a, The measured spin diffusion length as a function of temperature for two samples containing organic spacer layers of thicknesses 26 nm and 33 nm. The error bars accrue from the ± 5 nm uncertainty in the organic layer thickness in each case. **b**, The spin relaxation time as a function of temperature. The two curves correspond to the maximum and minimum values at any temperature. The large difference between the maximum and minimum values is entirely due to the two orders of magnitude spread in the reported mobility of carriers in AlQ₃.

There are four major spin relaxation mechanisms in solids: the D'yakonov–Perel' (D–P)²¹, the Elliott–Yafet (E–Y)²², the hyperfine interaction between nuclear and carrier (electron or hole) spins²³, and the Bir–Aronov–Pikus (B–A–P) mechanism²⁴.

The B–A–P mechanism is absent in unipolar transport, where only one type of charge carrier, either electrons or holes, carries current. The hyperfine interaction can be strong in a molecule like AlQ₃ (ref. 25), but is ineffective in causing spin relaxation because transport in a π -conjugated molecule like AlQ₃ takes place mostly through molecular states localized over the carbon atoms, which have no nuclear spin²⁶. That then leaves the D–P and the E–Y mechanisms as likely candidates for the spin relaxation mechanism in AlQ₃. The spin relaxation rate due to the D–P mechanism has a direct dependence on the carrier mobility²¹, but the spin relaxation rate due to the E–Y mechanism has an inverse dependence on the carrier mobility²². This is true of both organics and inorganics. In a nanowire of AlQ₃, which is a short-stranded organic molecule (not a long-chain polymer), there is no plausible reason for the mobility to increase significantly over the bulk value, but there is a strong possibility that it will decrease for the following reason. Nanowires have a larger surface-to-volume ratio than bulk or thin films. The charged surface states cause additional Coulomb scattering, which can reduce the carrier mobility significantly. In our nanowires, which are hosted in an alumina matrix, there are roughly 10^{13} cm⁻² surface states²⁷. Therefore, we believe that the mobility has decreased in the nanowire. In that case, the observation that the spin relaxation rate has increased suggests strongly that the E–Y mechanism is dominant. However, because we cannot

independently confirm that mobility has decreased in our nanowires, we cannot establish unequivocally that the E-Y mechanism is dominant. We can only say that it is strongly suggested.

From the spin diffusion lengths, we can deduce the spin relaxation times $\tau_s(T)$ as described in the Methods section. These results are plotted as a function of temperature in Fig. 4b. The two curves give the maximum and minimum values of $\tau_s(T)$. They range from few milliseconds to over 1 second at 1.9 K (the spread in the range is entirely due to the spread in the reported value of mobility in Alq₃). These are among the longest spin relaxation times reported in any system.

In conclusion, we have demonstrated that the spin relaxation time in organics is exceptionally long and relatively temperature-independent. This establishes organic semiconductors as a very viable platform for spintronics, particularly opto-spintronic devices such as spin-enhanced organic light-emitting diodes²⁸, where the spin relaxation time must exceed the radiation recombination lifetime of excitons in order for the efficiency to increase. We have also identified the likely dominant spin relaxation mechanism in the organic.

METHODS

FABRICATION OF NANOWIRE SPIN VALVES

The nanowires were produced within the 50-nm-diameter pores of an anodic alumina film. The film was produced by first electropolishing and then anodizing a 0.1-mm-thick aluminium foil in 0.3 M oxalic acid at a d.c. voltage of 40 V at room temperature. Anodization resulted in the formation of a porous alumina film on the surface of the foil, which was $\sim 1 \mu\text{m}$ thick and contained a well-ordered hexagonal close-packed array of 50-nm-diameter pores. The alumina barrier layer at the bottom of the pores was removed by a reverse polarity etching. Nickel was then electrodeposited selectively within the pores from a solution of NiSO₄·6H₂O using a d.c. voltage of 1.5 V. The nickel layer was ~ 500 nm thick based on our calibration. Next, Alq₃ was evaporated on the porous film through a mask with a window of area 1 mm² in a vacuum of 10⁻⁷ torr. The layer thickness was monitored with a crystal oscillator. The Alq₃ seeped into the pores by capillary action and reached the nickel. The fact that Alq₃ is a short-stranded organic of low molecular weight was helpful in transporting it inside the pores. Finally, cobalt was evaporated on the top without breaking vacuum (as in ref. 1). This results in the structure of Fig. 1.

For electrical measurements, we attached two gold wires to the top cobalt and the bottom aluminium layers using silver paste. Magnetoresistance of the structure was measured in a Quantum Design Physical Property Measurement System, consisting of a superconducting solenoid generating a magnetic field within a variable-temperature liquid helium cryostat.

CALCULATION OF SPIN RELAXATION TIME

It is possible to estimate the temperature-dependent spin relaxation time $\tau_s(T)$ from the spin diffusion length λ_T using the relation $\tau_s(T) = \lambda_T^2/D(T) = e\lambda_T^2/kT\mu(T)$, where $\mu(T)$ is the temperature-dependent drift mobility¹⁷. Based on available data²⁹, the mobility in our structures has been estimated to be $2 \times 10^{-8} - 2 \times 10^{-10} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Assuming that the mobility is temperature independent (which it should be if it is determined mainly by elastic Coulomb scattering), we have calculated the spin relaxation time $\tau_s(T)$ from the relation $\tau_s(T) = e\lambda_T^2/kT\mu$. These results are plotted in Fig. 4b.

Received 2 August 2006; accepted 13 February 2007; published 18 March 2007.

References

- Xiong, Z. H., Wu D., Vardeny Z. V. & Shi, J. Giant magnetoresistance in organic spin valves. *Nature* **427**, 821–824 (2004).
- Dediu, V., Murgia, M., Maticotta, F. C., Taliani C. & Barbanera, S. Room temperature spin polarized injection in organic semiconductor. *Solid State Commun.* **122**, 181–184 (2002).
- Forrest, S., Burrows, P. & Thompson, M. The dawn of organic electronics. *IEEE Spectr.* **37**, 29–34 (Aug 2000).
- Petta, J. R., Slater, S. K. & Ralph, D. C. Spin dependent transport in molecular tunnel junctions. *Phys. Rev. Lett.* **93**, 136601 (2004).
- Ruden, R. P. & Smith, D. L. Theory of spin injection into conjugated organic semiconductors. *J. Appl. Phys.* **95**, 4898–4904 (2004).
- Yu, Z. G., Berding, M. A. & Krishnamurthy, S. Spin drift, spin precession and magnetoresistance of non-collinear magnet–polymer–magnet structures. *Phys. Rev. B* **71**, 060408(R) (2005).
- Rocha, A. R., Garcia-Suarez, V. M., Bailey, S. W., Lambert, C. J., Ferrer, J. & Sanvito, S. Towards molecular spintronics. *Nature Mater.* **4**, 335–339 (2005).
- Pati, R., Senapati L., Ajayan, P. M. & Nayak, S. K. First principles calculations of spin polarized electron transport in a molecular wire: Molecular spin valve. *Phys. Rev. B* **68**, 100407(R) (2003).
- Zheng, M. *et al.* Magnetic properties of Ni nanowires in self assembled arrays. *Phys. Rev. B* **62**, 12282–12286 (2000).
- Francis, T. L., Mermer, O., Veeraraghavan, G. & Wohlgenannt, M. Large magnetoresistance at room temperature in semiconducting polymer sandwich devices. *New J. Phys.* **6**, 185 (2004).
- Mermer, O., Veeraraghavan, G., Francis, T. L. & Wohlgenannt, M. Large magnetoresistance at room temperature in small molecular weight organic semiconductor sandwich devices. *Solid State Commun.* **134**, 631–636 (2005).
- Pramanik, S., Bandyopadhyay, S., Garre, K. & Cahay, M. Normal and inverse spin valve effect in organic semiconductor nanowires and the background magnetoresistance. *Phys. Rev. B* **74**, 235329 (2006).
- Zeng, H. *et al.* Magnetic properties of self assembled Co nanowires of varying length and diameter. *J. Appl. Phys.* **87**, 4718–4720 (2000).
- McGuire T. I. & Potter, R. I. Anisotropic magnetoresistance in ferromagnetic 3d alloys. *IEEE Trans. Magn.* **11**, 1018–1038 (1975).
- Ohgai, T. *et al.* Template synthesis and magnetoresistance property of Ni and Co single nanowires electrodeposited into nanopores with a wide range of aspect ratios. *J. Phys. D* **36**, 3109–3114 (2003).
- Xie, S. J., Ahn, K. H., Smith, D. L., Bishop, A. R. & Saxena, A., Ground state properties of ferromagnetic metal/conjugated polymer interfaces. *Phys. Rev. B* **67**, 125202 (2003).
- Saikin, S. A drift-diffusion model for spin-polarized transport in a two-dimensional non-degenerate electron gas controlled by spin orbit interaction. *J. Phys. Condens. Matter* **16**, 5071–5081 (2004).
- Julliere, M. Tunneling between ferromagnetic films. *Phys. Lett. A* **54**, 225–226 (1975).
- Tsymbal, E. Y., Mryasov, O. N. & LeClair, P. R. Spin dependent tunneling in magnetic tunnel junctions. *J. Phys. Condens. Matter* **15**, R109–R142 (2003).
- Zahid, F., Ghosh, A. W., Paulsson, M., Polizzi, E. & Datta, S. Charging induced asymmetry in molecular conductors. *Phys. Rev. B* **70**, 245317 (2004).
- D'yakov, M. I. & Perel', V. I. Orientation of electrons associated with the interband absorption of light in semiconductors. *Sov. Phys. JETP* **33**, 1053–1059 (1971).
- Elliott, R. J. Theory of the effect of spin orbit coupling on magnetic resonance in some semiconductors. *Phys. Rev.* **96**, 266–279 (1954).
- Abraham, A. *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, 1961).
- Bir, G. L., Aronov, A. G. & Pikus, G. E. Spin relaxation of electrons due to scattering by holes. *Sov. Phys. JETP* **42**, 705–712 (1976).
- Sheng, Y. *et al.* Hyperfine interaction and magnetoresistance in organic semiconductors. *Phys. Rev. B* **74**, 045213 (2006).
- Sanvito, S. & Rocha, A. R. Molecular-spintronics: the art of driving spin through molecules. Preprint at <http://arxiv.org/cond-mat/0605239> (2006).
- Pokalyakin, V. *et al.* Proposed model for bistability in nanowire nonvolatile memory. *J. Appl. Phys.* **97**, 124306 (2005).
- Salis, G., Alvarado, S. F., Tschudy, M., Brunschwiler T. & Allenspach, R. Hysteretic electroluminescence in organic light-emitting diodes for spin injection. *Phys. Rev. B* **70**, 085203 (2004).
- Chen, B. J. *et al.* Electron drift mobility and electroluminescent efficiency of tris(8-hydroxyquinolinolato) aluminum. *Appl. Phys. Lett.* **75**, 4010–4012 (1999).

Acknowledgements

This work is supported by the US Air Force Office of Scientific Research under grant FA9550-04-1-0261, by the National Science Foundation under grant ECS-0608854 and by the US Department of Energy under grant DE-AC02-98CH10886 (subcontract from Brookhaven National Laboratory). Correspondence and requests for materials should be addressed to S.B.

Author contributions

S.B., S.Pr. and M.C. conceived and designed the experiments, S.Pr., C.G.S. and S.Pa conducted the experiments, S.Pr. and K.G. fabricated the structures and S.B. wrote the paper.

Competing financial interests

The authors declare that they have no competing financial interests.

Reprints and permission information is available online at <http://npg.nature.com/reprintsandpermissions/>