

## Applying Large-Area Molecular Technology to Improve Magnetoresistive Performance of Hybrid Molecular Spin Valves

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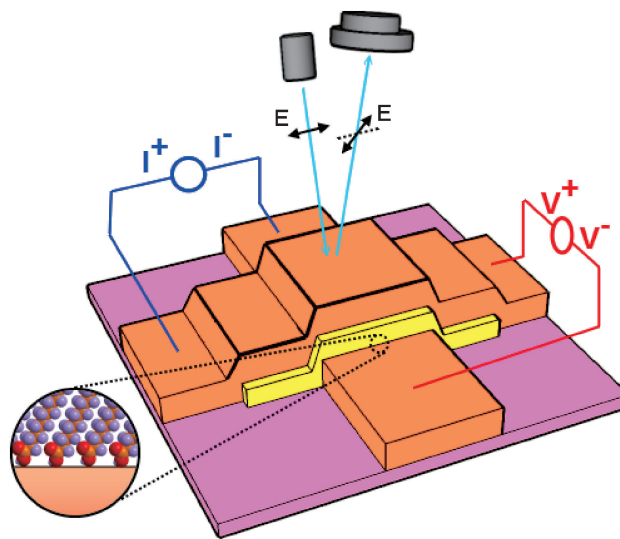
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Applying molecular-level technique to the construction of molecular spin valves is a challenging issue in organic spintronics, in which the magnetoresistive performance is highly sensitive to the device's local contact geometry. Here, we propose a molecular spin-valve design of large-area molecular junction to reduce the geometrical impact. Room-temperature tunneling magnetoresistance and well-defined parallel/antiparallel states are achieved in the spin valve with a molecular spacer. The results hold promise for the development of future molecular-level nonvolatile electronic devices. © 2012 The Japan Society of Applied Physics

The interdisciplinary nature of the fast-growing organic spintronics has led to the merger of spintronics and organic electronics, two frontier research areas of the day.<sup>1)</sup> Due to their mechanical and electrical flexibilities, the participation of organic materials in spintronics opens up an alternative direction for future device applications. Among the prototype device designs, the organic spin valve is the most promising kind, which adopts the concept of the conventional pseudo spin valve with two ferromagnetic (FM) layers of different coercivities and a spacer layer made of organic material.<sup>2)</sup> Alongside the pursuit of technological applications, there are also important fundamental issues to address in organic spintronics such as the probing of spin-polarized carriers in organic materials and spin polarization through organic molecules.<sup>3-5)</sup> Throughout the development of organic spintronics, many exciting findings have been uncovered, e.g., the bistability of magnetoresistance (MR) in organic spin valves<sup>6)</sup> and the isotope effect in polymeric spintronic devices.<sup>7)</sup> Recently, the involvement of evaporated small molecules and coated polymers in organic spin valves has attracted much attention,<sup>8,9)</sup> and some remarkable device structures have been proposed.<sup>10)</sup> Despite all the excitement, it is still challenging to construct spintronic devices using molecular-level techniques.<sup>11,12)</sup>

Fortunately, the vast studies of molecular electronics over the last decades have set a solid background for making molecular-level electronic devices,<sup>13)</sup> and the development of such fine tools as scanning tunneling microscopy has made the study of molecular spin transport possible.<sup>14)</sup> Recent attempts to combine molecular electronics and FM materials have led to the successful fabrication of molecular-level spin valves with self-assembled monolayers (SAMs) inside the nanopores.<sup>15)</sup> However, spin valves of such level exhibit complicated MR behavior due to the local contact geometry issue. A similar problem has been reported in the in-plane carbon nanotube (CNT) spin valves,<sup>16)</sup> which could be solved by depositing CNT above the FM layer to obtain well-defined parallel/antiparallel magnetization states.<sup>17)</sup> Nevertheless, such a method is not applicable to perpendicular-type molecular spin valves. In order to reduce the local contact geometry effect, we propose in this study the strategy of making a large-area molecular junction using the Langmuir–Blodgett (LB) technique,<sup>18)</sup> which has been

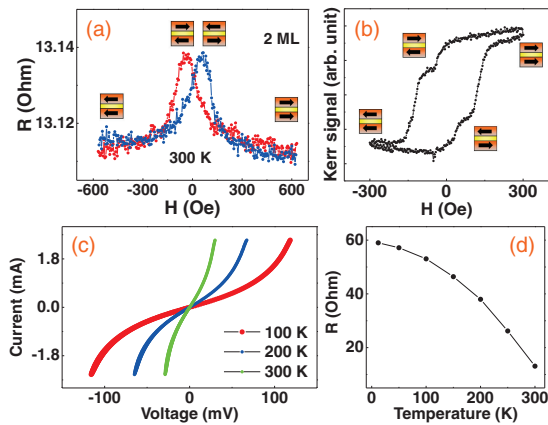


**Fig. 1.** Schematic of an LB-film-based molecular spin valve with the setups of MOKE and four-probe measurement for magnetic and transport characterizations, respectively.

demonstrated to form well-structured molecular devices.<sup>19)</sup> The strategy leads to a characteristic MR behavior and well-defined parallel/antiparallel magnetization states at room temperature in our molecular-level spin valves.

Figure 1 shows the schematic of our molecular spin-valve design that consists of two crossed FM electrodes separated by a thin layer of organic molecules,<sup>20)</sup> with a junction area of  $\sim 120 \times 120 \mu\text{m}^2$  defined by the overlap of the electrodes. The sequence of the layered structure (from bottom to top) is NiFe (22 nm)/CoFe (15 nm)/organic LB film/CoFe (30 nm), in which the combination of NiFe/CoFe acts as the soft FM layer whereas the capping CoFe acts as the hard layer.<sup>21)</sup> The use of NiFe/CoFe is also for the enhancement of spin polarization in the soft FM layer, as has been demonstrated in our previous works of oxide magnetic tunnel junctions (MTJs).<sup>21)</sup> The FM layers were made by sputtering and patterned by contact masks in a high-vacuum chamber with a base pressure of  $\sim 5 \times 10^{-8}$  mbar, whereas the organic molecules were constructed by LB processes,<sup>18)</sup> in which an organic “LB film” was formed in the KSV Mini-through System using 2 : 1 mixed stearic acid (SA) and bis(ethyl-enedithio)-tetrathiafulvalene (BEDT-TTF). By holding the

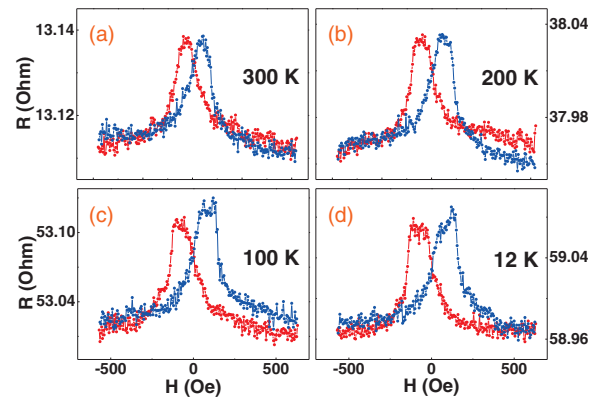
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**Fig. 2.** (a) RT TMR curve and (b) hysteresis loop of a molecular spin valve with 2-ML LB-film spacer. (c)  $I$ - $V$  curves of various temperatures and (d) zero-field resistance as a function of temperature, for a molecular spin valve with 2-ML LB-film spacer.

surface pressure of the condensed phase through a feedback system, LB films can be transferred onto cleaned glass substrates (with or without the FM underlayer) simply by dipping and pulling the substrates off the solvent contained in the KSV tank. Repeating this transfer process leads to the formation of layer-by-layer molecular thin film whose ordering can be verified on the basis of the contact angle between a water drop and the surface of the LB film (demonstrated in our previous work).<sup>22)</sup> After drying the LB films in air for several hours, the substrates holding the FM underlayers and the LB films were transferred back into the vacuum chamber for the capping of the top FM layers to form the complete molecular spin valves. The magnetic and transport properties of the spin valves were characterized on the basis of the magneto-optical Kerr effect (MOKE) and the four-probe measurement technique, respectively, as illustrated in Fig. 1.

Resistive measurements with field cycling exhibit a clear tunneling magnetoresistance (TMR) effect at room temperature (RT) in our molecular spin valve with a 2-monolayer (ML) LB-film spacer, as shown in Fig. 2(a). Figure 2(b) shows the MOKE hysteresis loop of the same device, in which the coercivities corresponding to the soft NiFe/CoFe and the hard CoFe layers are found to be around 35 and 110 Oe, respectively. The two-step characteristic of the curves is in agreement with the variation of the resistance. The device is electrically shortened if we intentionally made the spin valve following the same procedure but without holding the surface pressure during the LB processes (therefore, no LB film is transferred). The result suggests that the observed TMR effect is not likely due to any process-induced contamination. In current-perpendicular-to-the-plane (CPP)-type tunnel junction measurement using four-probe technique, the measured resistance is typically dominated by the junction rather than by the electrodes. Therefore the relatively small change of electrode resistance contributed by the anisotropic magnetoresistance (AMR) or the local Hall effect is generally negligible. To verify the AMR contribution, a simple test is made by rotating the magnetic field 90 degrees from the magnetization direction. The result shows no sign change and thus the possibility of AMR effect is excluded. In comparison with the previously

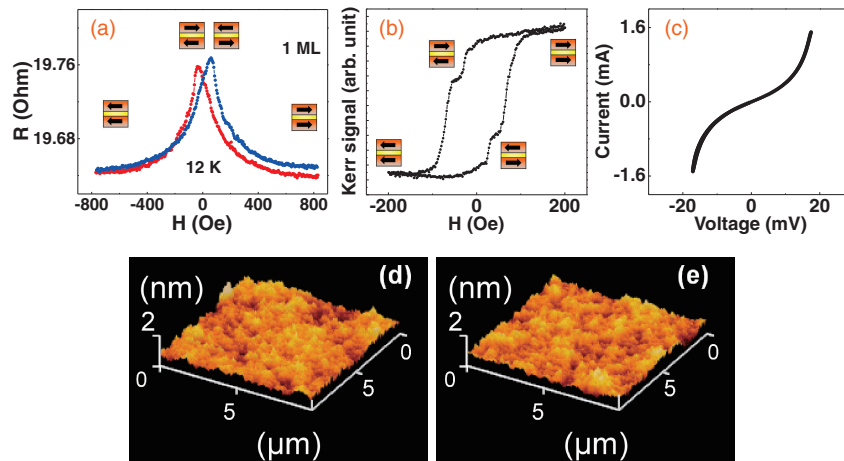


**Fig. 3.** TMR loops of a molecular spin valve with 2-ML LB-film spacer at different temperatures.

reported low-temperature TMR effect observed in the nanopore molecular spin valves,<sup>15)</sup> our experiments reveal not only the RT TMR effect, but also distinct parallel/antiparallel magnetization states from a large-area molecular spin valve.

Figure 2(c) shows the current-voltage ( $I$ - $V$ ) curves of the molecular spin valve with a 2-ML LB-film spacer at various temperatures. The curves display nonlinearity and the shape of the curves widens upon lowering the temperature. Figure 2(d) plots the zero-field resistance of the device as a function of temperature. The junction resistance decreases with increasing temperature. The  $I$ - $V$  characteristics indicate that the layered structure of the LB-film-based spin valve is well-established to form an effective molecular magnetic tunnel junction. The thermal impact on the TMR effect of the 2-ML LB-film molecular spin valve is given in Figs. 3(a)-3(d), where the magnetoresistive loops were taken at four different temperatures. The features have come to our attention from these plots: the shape of the TMR peaks is more rectangular with a slightly larger peak width at lower temperatures, and that may be most likely caused by the temperature effect on magnetic states.

Thus, we have demonstrated a clear TMR effect at temperature ranging from 12 K to RT in a molecular spin valve containing a 2-ML LB film. What happens if we reduce the LB film thickness to 1 ML? The magnetoresistive behavior of the 1-ML spin valve is more complicated (possibly due to a magnetic property change impacted by the thinner LB film, as reported in our previous work),<sup>22)</sup> and we are able to obtain a convincing TMR effect only at 12 K, as indicated in Fig. 4(a). Figures 4(b) and 4(c) show the two-step feature of the hysteresis loop and the nonlinearity of the  $I$ - $V$  curve, respectively, confirming that the molecular magnetic tunnel junction with the 1-ML LB-film spacer is also well established with consistent magnetic states. We further apply model fitting to the  $I$ - $V$  curve to obtain the effective barrier widths of the LB-film spin valves.<sup>23)</sup> Such a method has often been used to characterize monolayer-level molecular electronic devices. Unlike MTJs with mechanically hard oxide barriers whose widths can be revealed in the transmission electron microscopy (TEM) images,<sup>24)</sup> soft molecular junctions are easily damaged during the TEM sample preparation, and hence, an indirect fitting method is needed.<sup>25)</sup> Our fitting results suggest that the effective



**Fig. 4.** (a) TMR loop of a molecular spin valve with 1-ML LB-film spacer measured at 12 K. (b) Spin-valve's hysteresis loop. (c)  $I$ - $V$  curve. AFM morphological images of (d) 1- and (e) 2-ML LB films made on FM underlayers. In both cases, the rms roughness is about 0.2 nm.

barrier widths are 1.75 nm for the 1-ML and 3.68 nm for the 2-ML spin valves, which are consistent with the thicknesses estimated on the basis of the ML number. Moreover, the surface morphologies of the LB films, as determined by atomic force microscopy (AFM), are shown respectively in Figs. 4(d) and 4(e) for 1- and 2-ML LB films made on FM underlayers without the capping ferromagnets. The root-mean-square (rms) roughness of both films (measured to be 0.2 nm) reveals a significant improvement over the previously reported values.<sup>1,8)</sup>

Organic spin valves with RT TMR performance are highly desirable for the development of spintronic devices used in daily life. Methods to achieve such an RT effect include the incorporation of polymer or graphene as spacer materials.<sup>9,26)</sup> For CNT spin valves, the TMR effect is observed only at low temperatures;<sup>16,17)</sup> for spin valves with a small-molecule spacer, a number of reports have claimed to reach a RT TMR effect by inserting an additional oxide layer.<sup>5,27)</sup> Several reported thin-films containing fullerene molecules with embedded FM particles also show RT MR effect.<sup>28–31)</sup> To date, most reported organic spin valves with a pure organic spacer (small molecules) achieved the TMR effect under cryogenic condition.<sup>1,8,15)</sup> Our experimental results, on the other hand, show that the TMR effect at RT can still be observed in the LB-film-based spin valve with a spacer as thin as 2 ML without the insertion of any oxide layer. In particular, the effect is achieved in the spin valve made with a large junction area through molecular-level techniques. Thus, the strategy of large junction area is proven effective for solving the complex magnetization state issues encountered in previous works.<sup>15)</sup> Unlike other LB film works that exhibit peculiar MR behavior,<sup>32)</sup> our spin valves show clear and well-defined parallel/antiparallel magnetization states. As a final remark, the specific  $RA$  (product of resistance and junction area) of our LB-film spin valve is consistent with that of other reported molecular-level spin valves;<sup>15)</sup> and the resistance is also consistent with the reported values of other LB-film devices.<sup>32)</sup>

In conclusion, we have demonstrated the room-temperature TMR effect in a molecular spin valve containing a monolayer-level (2-ML) LB-film spacer. The layer-by-layer

growth of the LB film is shown to be morphologically uniform. The  $I$ - $V$  and hysteresis characterizations reveal a well-defined junction structure and magnetic states. The prominent MR behavior implies that the combination of a large-junction-area strategy with LB-film technique is promising for solving the local geometry problem, which is particularly critical for molecular-level spin valves. These findings support the possibility of constructing future non-volatile organic spintronic devices based on molecular tunnel junctions.

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- 1) Z. H. Xiong *et al.*: *Nature* **427** (2004) 821.
- 2) V. A. Dediu *et al.*: *Nat. Mater.* **8** (2009) 707.
- 3) A. J. Drew *et al.*: *Nat. Mater.* **8** (2009) 109.
- 4) M. Cinchetti *et al.*: *Nat. Mater.* **8** (2009) 115.
- 5) T. S. Santos *et al.*: *Phys. Rev. Lett.* **98** (2007) 016601.
- 6) L. E. Hueso *et al.*: *Adv. Mater.* **19** (2007) 2639.
- 7) T. D. Nguyen *et al.*: *Nat. Mater.* **9** (2010) 345.
- 8) W. Xu *et al.*: *Appl. Phys. Lett.* **90** (2007) 072506.
- 9) S. Majumdar *et al.*: *Appl. Phys. Lett.* **89** (2006) 122114.
- 10) S. Pramanik *et al.*: *Nat. Nanotechnol.* **2** (2007) 216.
- 11) A. R. Rocha *et al.*: *Nat. Mater.* **4** (2005) 335.
- 12) S. Sanvito: *Chem. Soc. Rev.* **40** (2011) 3336.
- 13) N. J. Tao: *Nat. Nanotechnol.* **1** (2006) 173.
- 14) S. Schmaus *et al.*: *Nat. Nanotechnol.* **6** (2011) 185.
- 15) J. R. Petta *et al.*: *Phys. Rev. Lett.* **93** (2004) 136601.
- 16) K. Tsukagoshi *et al.*: *Nature* **401** (1999) 572.
- 17) L. E. Hueso *et al.*: *Nature* **445** (2007) 410.
- 18) D. R. Talham: *Chem. Rev.* **104** (2004) 5479.
- 19) C. P. Collier *et al.*: *Science* **285** (1999) 391.
- 20) A. Fert: *Rev. Mod. Phys.* **80** (2008) 1517.
- 21) Y.-M. Chang *et al.*: *Phys. Rev. B* **79** (2009) 012401.
- 22) J.-C. Tai *et al.*: *Appl. Phys. Lett.* **96** (2010) 262502.
- 23) J. G. Simmons: *J. Appl. Phys.* **34** (1963) 1793.
- 24) C. H. Ho *et al.*: *J. Appl. Phys.* **90** (2001) 6222.
- 25) J. M. Beebe *et al.*: *Phys. Rev. Lett.* **97** (2006) 026801.
- 26) N. Tombros *et al.*: *Nature* **448** (2007) 571.
- 27) V. Dediu *et al.*: *Phys. Rev. B* **78** (2008) 115203.
- 28) S. Sakai *et al.*: *Appl. Phys. Lett.* **89** (2006) 113118.
- 29) S. Sakai *et al.*: *Appl. Phys. Lett.* **91** (2007) 242104.
- 30) S. Miwa *et al.*: *Jpn. J. Appl. Phys.* **45** (2006) L717.
- 31) S. Miwa *et al.*: *Phys. Rev. B* **76** (2007) 214414.
- 32) Y. Ando *et al.*: *Thin Solid Films* **331** (1998) 158.