A multifunctional molecular spintronic platform with magnetoresistive and memristive responses via a self-assembled monolayer

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ABSTRACT

We report the spin-dependent transport and the I-V hysteretic characteristics in molecular-level organic spin valves containing a self-assembled-monolayer (SAM) barrier of 1,4 benzenedimethanethiol (BDMT). X-ray photoelectron spectroscopy confirms the establishment of an ordered self-assembled monolayer of BDMT with the phosphonic groups coordinated onto the ferromagnet surface. The magnetoresistive (MR) and the I-V curves characterize the transport properties of the SAM-based organic spin valves, which exhibit both types of non-volatile memory switching, i.e., the magnetoresistive and the memristive switching. The results reveal the possibility of integrating organic SAM into the future multifunctional molecular-level spintronic device applications.

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INTRODUCTION

The fast development of organic/inorganic hybrid heterojunctions opens up new possibilities of integrating multi-functionalities into modern electronic devices, which were previously not feasible by the conventional metallic/inorganic hetero-junction structure. While simple organic/metallic junctions have been demonstrated to be highly applicable to a variety of electronics,^{1–3} novel organic/ferromagnetic (FM) hetero-structures, which combine the versatility of organic materials and the spin-degree of freedom of ferromagnets, have just been realized in a number of spintronic applications, such as organic spin valve (OSV), spin-enhanced organic lightemitting diode (OLED), and photovoltaic device.^{4–7} However, the creation of such hetero-junctions with well-defined organic/FM interfaces, which are sensitively impacted by the growth condition and the materials' compatibility, is a great challenge.^{8–11} Upon the contact of organic and FM materials, issues like the molecular ordering and the interlayer diffusion and interaction not only affect the transport properties of the junction but also entangle with one another, complicating the investigation.^{9,12,13} Recently, the techniques of the Langmuir-Blodgett (LB) film and the self-assembled monolayer (SAM) with a large-area junction have been proposed for solving the complicated active-layer problem and have been adopted in several nano-scale devices.^{14–16} The incorporation of SAM is technologically advantageous not only because of the potential for establishing a down-scaling, bottom-up building block but also because of the flexibility of molecule choices, selective growth, and tailored functionality. Nevertheless, the studies of embedding SAM into organic spintronic devices are only preliminary, and a few examples can be seen in molecular OSV with nano-pore structures.^{17–19}

In this work, we report the spin-dependent transport properties of a molecular-level OSV device containing a well-ordered organic-SAM layer of 1,4 benzenedimethanethiol (BDMT) of thickness \approx 1 nm, as confirmed by the X-ray photoelectron spectroscopy (XPS) analysis. In addition to the typical magnetoresistive (MR) effect, the device also exhibits non-volatile electrical memristive characteristics, leading to the possibility of implanting multiple functions into a single device. The non-volatile electrical resistive-switching effect, or noted as the memristive effect, has received intensive attention in the past few years due to the potential for memory applications in modern electronic devices.^{20,21} The effect is characterized by the non-volatile hysteresis of junction resistance (called the memristance) upon the cycling of the applied current or voltage. Depending on the type of materials, memristance can be of different origins. For example, the hysteretic current-voltage characteristics demonstrated by the semiconductor-based memristors are attributed to the interaction of electronic and ionic transports driven by the external voltage at the oxide active layer.^{22,23} This non-volatile effect provides a playground for developing electronics with different and complementary operations,^{24–26} since a multifunctional device (with electrical, magnetic, and/or optical inputs) on the same chip offers more external control options and in the meantime simplifies its hierarchical structure. The memristive effect has also been reported in organic devices either in the form of thin films or containing a self-assembled monolayer.^{27,28} Nevertheless, reports of such multifunctional SAM device applications are still quite limited. Here, we investigate the mechanism of charge transport in a SAM-based OSV system by fitting the I-V curves with the Simmons' formula, and the results infer that charge trapping at the organic-SAM/FM interface is mainly responsible for the hysteretic I-V behavior. We hope that the work is beneficial to the development of future multifunctional, molecular-level organic spintronic devices.

EXPERIMENT

The structure of the SAM-based organic spin valve is stacked in the sequence of NiFe (15 nm)/CoFe (10 nm)/BDMT (1 nm)/AlOr (1 nm)/CoFe (35 nm) and patterned in a crossbar configuration, with the bottom NiFe/CoFe layer designed as the soft ferromagnetic (FM) electrode and the top CoFe as the hard FM electrode [see Fig. 1(a) for the schematic illustration]. The entire fabrication process was executed in a UHV sputtering chamber except the part of grafting the BDMT self-assembled monolayer onto the bottom FM electrode, which was accomplished by immersing the substrate (with the bottom electrode layer) into a freshly N2 bubbling degassed 5 mM solution of n-Decane for 24 h. The sample was then rinsed with the same solution and dried under a stream of nitrogen gas before transporting back into the UHV chamber for the deposition of the capping AlO_x and top electrode (TE) layers. The junction resistance and the MR effect, measured in the Current-Perpendicular-to-the-Plane (CPP) configuration with the applied magnetic field parallel to the bottom electrode, were obtained by the four-point-probe method. The electronic properties of the BDMT-SAM/FM interface were investigated on a separate set of samples made intentionally without the capping AlO_x and the CoFe layers, but under the identical conditions as the regular OSV samples, using XPS at Beamline 09A1 of the National Synchrotron Radiation



FIG. 1. (a) Structural schematic of the tri-layered molecular-level organic spinvalve (OSV) dusted with partially oxidized alumina at the top organic semiconductor (OSC)/FM interface. (b) The XPS S 2p and C 1s spectra of the BDMT self-assembled monolayer grafted onto the CoFe underlayer. The open circles indicate the measured XPS data, whereas the orange curves are the best fits obtained by superimposing the individual components.

Research Center (NSRRC) in Taiwan, with a 0.12 eV energy resolution set by the pass energy of 5.85 eV of the Hemispherical Sector Analyzer (HSA). The XPS spectra were analyzed by the convolution of Lorentzian and Gaussian contributions, i.e., the so-called Voigt profile, using the UNFIT simulation program.

RESULTS AND DISCUSSION

Figure 1(b) shows the C 1s and S 2p core-level XPS spectra of the BDMT self-assembled monolayer (SAM) grafted onto CoFe. Since XPS is a relatively surface-sensitive technique with a probing depth typically less than 2 nm, the BDMT SAM used in the XPS

study is therefore suitable for distinguishing the interface-bonded and the free-standing end groups. The S 2p spectrum shown in Fig. 1(b) has been normalized to the photon flux with the background signal subtracted. The spectrum reveals a good signal/noise (s/n) ratio of the synchrotron generated x-ray source and is fitted with the Voigt-doublet profiles. For each S 2p doublet, a 1.2 eV spin-orbit splitting and a 2:1 branching ratio between the 3/2 and the 1/2 components are adopted, with the peaks within each doublet assumed to be of the same width. The main doublet at 163.3 (S2), with a full-width-half-maximum (FWHM) of 0.87 eV, is associated with the unbound sulfur, i.e., sulfur not directly engaged in a thiolate molecule S-OH surface interaction, as, for example, the free thiol (SH) groups or the S-S bonds. The lower binding energy component at 162.4 (S1), with a FWHM of 0.87 eV, is assigned to the thiolate sulfur bound to the CoFe substrate. Note that the absence of higher binding energy components (above 166 eV)^{29,30} excludes the presence of oxidized sulfur species in the present SAM. The XPS spectra of Fe and Co taken on a control sample of NiFe/CoFe/SAM-BDMT/ AlO_x (identical OSV without the top electrode) exhibit no evident signs of oxidation, indicating that the CoFe surface remains mostly intact during the fabrication process.

Information on the establishment of a compact monolayer can be obtained by examining the S2/S1 (unbound/bound S) intensity ratio. In the present case, this ratio is 4.4, matching the value of 4 that is expected from a single layer of molecules standing upright.³¹ This ratio is noticeably less than the values 5.4–6.3 as obtained in BDMT films prepared by room-temperature dipping in solvents for 24 h.³¹ The result indicates that the preparation method adopted in this study yields a single-layer film, with the molecules presumably in a vertical configuration. The inset of Fig. 1(b) shows the presence of a single C 1 s structure with its maximum intensity located at 284.8 eV. The main photoemission contribution at 284.8 eV can be attributed to the aromatic carbon atoms and the carbon atoms in the methylene units, whereas the higher binding energy tail is likely related to the shake-up process that produces aromatic rings in the organic film.

For magneto-transport characterization, Fig. 2(a) shows the cycling of junction resistance with applied magnetic field, measured at a low-resistance state (LRS, see below) with a constant current of 10 μ A, for a SAM-based OSV. The resistance curves display the typical pseudo spin-valve type characteristics at room temperature (RT) with a magneto-resistive (MR) ratio of 0.25%, where the MR ratio is defined as

$$\frac{\Delta R}{R_P} = \frac{R_{AP} - R_P}{R_P},\tag{1}$$

with R_P and R_{AP} depicting the resistances when the magnetizations of the FM electrodes are in the parallel and antiparallel configurations, respectively. The MR ratio increases substantially at cryogenic temperatures, i.e., 1.9% at 100 K and 2.4% at 20 K, as seen in Fig. 2(a). The junction resistance itself increases by a factor of 2.3 when the temperature is decreased from RT to 20 K [see Fig. 2(b)], showing an agreement with the organic semiconductor behavior.^{13,32} To ensure that the MR effect is not resulted from the tunneling through the thin alumina layer, a control sample is made



FIG. 2. (a) Magnetoresistive curves at 20 K, 100 K, and 300 K and (b) the temperature dependence of the MR ratio (referenced to the right axis) and the junction resistance (normalized to the room-temperature resistance, referenced to the left axis) of a SAM-based organic spin valve. (c) The temperature dependence of the junction resistance of a control sample made without the SAM layer (see text). All data shown are measured at a constant current mode ($10 \mu A$) under LRS condition (see text).

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with an identical structure but without the organic SAM layer. Our previous XPS study on organic spin valves indicates that when the organic molecules are in direct contact with the ferromagnetic Co underlayer, a strong chemical interaction between Co and the molecular functional groups occurs, leading to the formation of a CoO complex that would suppress the spin injection from Co into the organic layer.⁹ The introduction of a thin AlO_x layer at the FM/organic interface blocked the chemical interaction and effectively restored the spin injection. Besides, in OSVs, the junction resistance and MR ratio depend strongly on temperature, whereas in oxide-based tunnel junctions, the dependence is less substantial. In the present study, the control sample shows a zero MR ratio and a junction resistance $\approx 20 \Omega$ at RT. Moreover, Fig. 2(c) reveals that the control sample's resistance follows the typical metallic behavior. These results indicate that the MR effect exhibited by the SAM-based OSV comes from the spin-dependent transport through the organic SAM layer rather than from the thin alumina layer (note that the OSV with SAM-BDMT shows no-broken junction resistance). In particular, the temperature dependence of the resistance suggests that the transport within the SAM layer is not a simple tunneling process, but rather a hopping process via localized states.

Figure 3(a) shows the room-temperature, zero-field I-V curves of the SAM-based organic spin valve with the top electrode being negative (i.e., current flows from bottom to top). The pinched hysteresis loop is the fingerprint of a memristive device. The device switches between the low-resistance state (LRS) and the high resistance state (HRS) upon current sweep; once the resistance is switched, the device remains in the same state until the opposite maximum current is reached. Compared to the I-V curves obtained from scanning tunneling microscopy (STM) measurements that show no hysteresis,33 the cause of intrinsic switching of the molecules can be eliminated. The pinched I-V hysteresis characteristic is the key to the application of resistive switching memory. Figure 3(b) shows the read-write-read-erase cycle when the SAM-based organic device is exposed to pulsed current where the write/read/erase current is set at 4 mA/1 mA/-4 mA and the pulse interval at 1 ms, respectively. During the cycling, the resistance is switched to HRS upon applying the write current, whereas a higher resistance state is obtained by applying the read current. The erase pulse brings the device back to LRS. Such characteristics can represent the basic logic elements, i.e., 0 and 1, of a memory device.

Figure 4(a) shows the I-V hysteresis loops of the SAM-based device at various temperatures. The opening of the hysteresis (i.e., the gap between HRS and LRS) becomes smaller as temperature decreases. This could be understood as that the number of electrons in the localized states decreases and also that the electrons cannot gain enough energy for hopping into the higher energy states. The inset of Fig. 4(b) shows the room-temperature I-V loops of the same sample at different looping ranges. The hysteresis opens wider at negative current as the looping range increases. This could be attributed to the increase of the intrinsic repulsive force induced by the higher trapping states upon increasing the negative current. To further prove that the resistance behavior is caused by the indirect tunneling process, we have compared the temperature dependence of the conductance in our samples with the one-dimensional hopping model described by the relation

$$G(T) \propto \exp(AT^{-1/2}), \tag{2}$$

where G, T, and A are the conductance, the temperature, and a constant related to the (bulk) inverse localization radius (lloc), respectively.³⁴ Figure 4(b) shows the fit of the conductance's temperature dependence of a SAM-based OSV using the model. Here, we have plotted $\log[G(T)-G(T=20 \text{ K})]$ [or $\log(\Delta G)$] as a function of $T^{-1/2}$. The data follow the linear dependence predicted by the model for two different temperature ranges, i.e., two different A constants with a transition temperature at 220 K. This implies that for different temperatures, the electronic states contributing to the conduction of OSV have different hopping probabilities through the localized states. Near room temperature (where l_{loc} is large), the conduction occurs mostly via inelastic and resonant tunneling, resulting in a strong G(T) dependence. At lower temperature (reduced l_{loc}), on the other hand, the contribution switches toward direct tunneling, and hence, the G(T) dependence is weaker. Thus, upon lowering the temperature, the inelastic-dominated transport



FIG. 3. (a) The room-temperature I-V hysteresis loop and (b) the read-writeerase cycles of the resistance response of a SAM-based OSV when exposed to 1 ms pulsed current.

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FIG. 4. (a) The I-V hysteresis loops of the OSV sample measured at different temperatures. The inset shows the RT I-V hysteresis loops of the same sample at different current ranges. (b) The dependence of the junction conductance with the inverse-square-root of temperature and the fits to a onedimensional hopping model. (c) A fit of the conductance-voltage curves to Simmons' model [Eq. (3)] at low bias voltage. The inset shows a fit of the curves to a power-law model at higher voltage. (d) Schematic energy diagrams describing the interface before (left) and after (right) a metal and an organic semiconductor contact each other.

diminishes while the hopping process is being suppressed, whereas the probability of direct tunneling increases.

To better understand the charge transport mechanism in the SAM-based organic spin valve, we further analyze the conductancevoltage curves by Simmons' model for the applied bias range. Depending on the bias voltage (V), with respect to the barrier height Φ_B/e , the type of electron tunneling through the SAM layer can be categorized into (1) direct ($V \le \Phi_B/e$), (2) trappingdependent ($V \approx \Phi_B/e$), and (3) Fowler-Nordheim (NF, $V \ge \Phi_B/e$) tunneling. At low bias voltage ($V \le \Phi_B/e$), the tunneling behavior through an insulating barrier can generally be described by Simmons' formula. Figure 4(c) shows that both the LRS and the HRS curves at low bias agree with Simmons' equation

$$G \cong G_0(1 + CV^2), \tag{3}$$

where G_0 is the equilibrium conductance and *C* is the barrier shape-related cubic coefficient. Based on the assumption of the model and the fitting result, direct tunneling across a rectangularlike barrier is suggested to be the primary transport mechanism for the range V ≤ 400 mV. At higher voltage [400 mV-520 mV, see the inset of Fig. 4(c)], the curves can be fitted by a power-law model G $\propto V^m$ with the exponent $m \geq 1$, indicating a trapping-dependent mechanism at this range.^{33,35,36} Previous studies have suggested that trapping-dependent transport in organic semiconductors is assisted by the interface states located near the midpoint of the semiconductor energy gap.^{37,38} By further increasing the applied bias (\geq 520 mV), deviation from the trapping-dependent mode is observed, which suggests a transition to the Fowler-Nordheim (FN) type tunneling (fitting not shown here). This is a field emissiontype tunneling resulted from the change of the effective barrier shape from rectangular-like to triangular-like in metal/insulator/ metal junctions when $V \geq \Phi_B/e$.³⁹ The transition from trappingdependent to FN tunneling is strongly field-dependent with a systematic decrease of tunneling distance as voltage increases and is more notable in the high resistance states [see the inset of Fig. 4(c)].

According to the aforementioned fitting results, we infer that the charges trapped at the SAM-BDMT/CoFe interface are the primary cause of the memristive effect. The asymmetric I-V characteristic suggests that trapping within the molecules is unlikely. Previous studies also indicated that interfacial trapping is mainly responsible for the dual-state situation in the I-V measurements.⁴ When a metal and an organic semiconductor are brought in contact, a disordered dipole layer often forms at the interface, which broadens the energy distribution of the localized states. Figure 4(d) shows schematically the energy diagram of a metallic/ organic bilayer system. The energies of the interfacial localized states are represented by a Gaussian distribution, assuming that a well-ordered dipole layer is formed between CoFe and SAM-BDMT. The transport scenario is therefore proposed as follows: in the low (negative) voltage regime, electrons are transported from the bottom electrode (BE) to the top electrode (TE) by direct tunneling and the resistance is in the low resistance state (LRS). As the (negative) voltage increases, the inelastic process

rises, and the number of electrons trapped in the interfacial localized states soars, creating a repulsive force. When the (negative) voltage is inversed, the resistance switches to the high-resistance state (HRS) since the Coulomb repulsion of the trapped electrons is now stronger. Upon the (negative) voltage decrease, more electrons hop into the BE than those from the TE into the localized states. The hopping process into the BE is easier due to the energy distribution of the states, and therefore, the resistance switches back to the LRS until the (positive) voltage reaches the switching threshold. Note that the MR effect is obtained only at LRS and there is no MR at HRS. This could be due to the interfacial dipole/localized states at HRS, which cause spin scattering/flipping, while the spinpolarized electrons transport through the SAM-BDMT layer.

CONCLUSION

In conclusion, we have demonstrated a reliable approach to contact a self-assembled molecular monolayer onto a ferromagnetic underlayer with the contact area larger than $150 \times 150 \,\mu\text{m}^2$, which forms the basis of a hybrid ferromagnetic/SAM/ferromagnetic organic spin valve. The OSV device exhibits both magnetoresistance and non-volatile resistive memory switching, with the ferromagnetic layers acting as a spin-polarized injector and a detector. The electronic transport of the system goes through sequential transitions from direct tunneling, trapping-dependent hopping, to Fowler-Nordheim tunneling at different stages of applied bias. The unique properties of OSV demonstrated in this study reveal the possibility of integrating SAM into future multi-functional molecular-level organic spintronic devices.

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