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Magnetoresistance in Organic Materials

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1. Introduction

Considerable attention has recently been paid to the active control of spin degrees of freedom in organic materials (OMs) because of their long spin relaxation time owing to their weak spin-orbit coupling. Although many studies concerning the magnetoresistance (MR) in spin-valve devices consisting of ferromagnetic metal (FM) /OM/FM sandwich structures have been reported [1] since a pioneering work on giant MR in organic spin-valves using thintris(8-hydroxyquinolinato)aluminum (Alq_3)[2], there is debate whether spins are just tunnelling between electrodes or are transported in OMs.

In order to clarify the spin injection and transport characteristics in OMs, we have prepared layered and planar type spin-valves based on single crystals, thin films and single molecules of OMs.

2. Experimental

Figure 1 shows a schematic of the layered devices studied. Epitaxial films of $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) and Co_2MnSi (CMS) were prepared on $SrTiO_3$ (100) and MgO (100) substrates, respectively, by a pulsed laser beam deposition method. Both LSMO and CMS show a half-metallic property with the Curie temperature of approximately 350 K and 985 K, respectively. Their crystal structure and magnetic properties were investigated with an X-ray diffractometer and a superconducting quantum interference device (SQUID), respectively. The typical dimension of the bottom electrode was 0.5 mm x 1.0 mm x 100 nm. Thin films of OMs including Alq_3, C_{60}, pentacene, N,N'–Bis (3-methylphenyl)-N,N'-bis(phenyl)-benzidine (TPD), and titanyl-phthalocyanine (TiOPc) were prepared onto the electrode by physical vapor deposition. Subsequently, thin layers of Co and Au were deposited to complete the spin-valve devices.

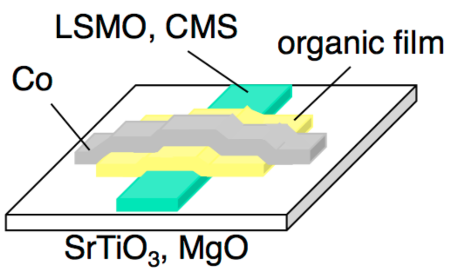

Fig. 1. Schematic of a layered device.

As for the planar-type devices, a 30-nm-thick Ni electrodes with a spacing of a few hundreds nm were prepared on Si substrates by electron beam lithography and electron beam deposition techniques. Thin single crystals of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) derivatives were placed on the electrodes.

The spin-valve characteristics of layered- and planar-type devices were measured under the magnetic field between -4000 Oe and 4000 Oe at the temperature range from -5 K to 300 K with a physical property measurement system (PPMS, Quantum Design Inc.).

For MR measurements of a single molecule, we adapted a mechanically controllable break junction (MCBJ) method with thin Ni electrodes as shown in Fig. 2. A pair of Au/Cr electrodes was prepared by conventional photolithography on a thin Si plate. Au and Ni layers were grown by electrochemical deposition on Au/Cr electrodes to form a nano contact of Ni. A droplet of mesitylene containing 1,4-benzendithole (BDT) was placed on the electrode and the MR of the single molecular junctions was measured under the magnetic field from -2000 Oe to 2000 Oe at room temperature.

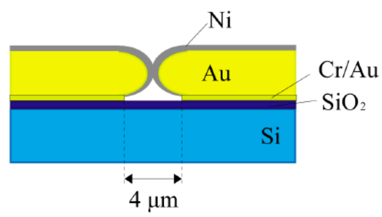

Fig. 2. Schematic of the Ni electrodes for single molecule spin-valves.

2. Results and Discussion

Layered-type Devices

Figures 3(a) and 3(b) show the MR loop of layered devices composed of thin and thick TiOPc films, respectively, with LSMO electrodes. The devices with thin TiOPc layers showed the inverse (negative) MR, while those with thick ones showed the normal (positive) MR. The devices based on pentacene and TPD showed the same behaviors. On the other hand, Alq_3- and C_{60}-based devices exhibited the inverse MR independently of their thicknesses, as is summarized in Table I.

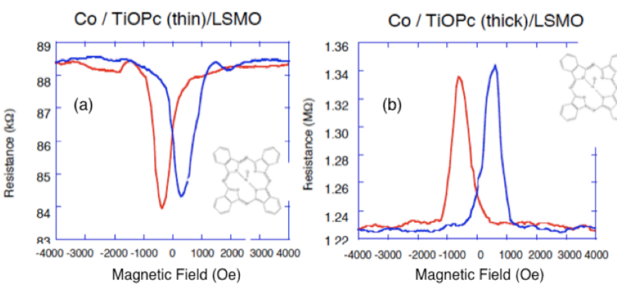

Fig. 3. MR of layered Co/TiOPc/LSMO structures (10K, 0.1V), (a) thin TiOPc, and (b) thick TiOPc.

Table I. Signs of MR in Co/OMs/LSMO devices

Material	Thin Layer	Thick Layer
TiOPc	inverse	normal
pentance	inverse	normal
TPD	inverse	normal
Alq_3	inverse	inverse
C_{60}	inverse	inverse

It is known that TiOPc, pentacene and TPD are hole transport materials. Alq_3 and C_{60} are usually used as electron transport materials. All devices with thin OMs layers showed inverse MR, indicating that the tunneling transport of spins is dominant. The devices based on thick films of hole transport OMs and electron transport ones showed normal and inverse MR, respectively. This indicates that highest occupied molecular orbitals in hole transport OMs and lowest unoccupied ones in electron transport OMs are involved in the spin transport.

Planar-type Devices

We have studied spin-valve characteristics of single crystals of molecular conductor with a nonlocal geometry, in which the electric current is separated from the spin current. The spin relaxation time was calculated to be approximately 10 ns which is longer than that in grapheme [3].

Single Molecule Devices

Figure 4(a) shows a MR loop observed for a Ni/BDT/Ni molecular junction at room temperature. The bias voltage was 10 mV and the magnetic field was applied orthogonal with respect to the current path. The formation of the molecular junction illustrated in Fig. 4(b) was confirmed by the observation of the plateau in the conductance transient curve. The MR ratios for Ni/BDT/Ni junctions were in the rage from 20% to 30% in the present experiment [4]. Figure 4(c) shows a MR loop for a Ni tunneling junction as shown schematically in Fig. 4(d). The gap between the electrodes was tuned to have almost the same electric resistance value as that for single molecular junctions (a few hundreds kΩ). The MR ratio was approximately 4%. The sign and ratio of MR for the tunnel junction was different from those for single molecular junctions, indicating that the coupling between a molecule and electrodes drastically affected to the MR behavior.

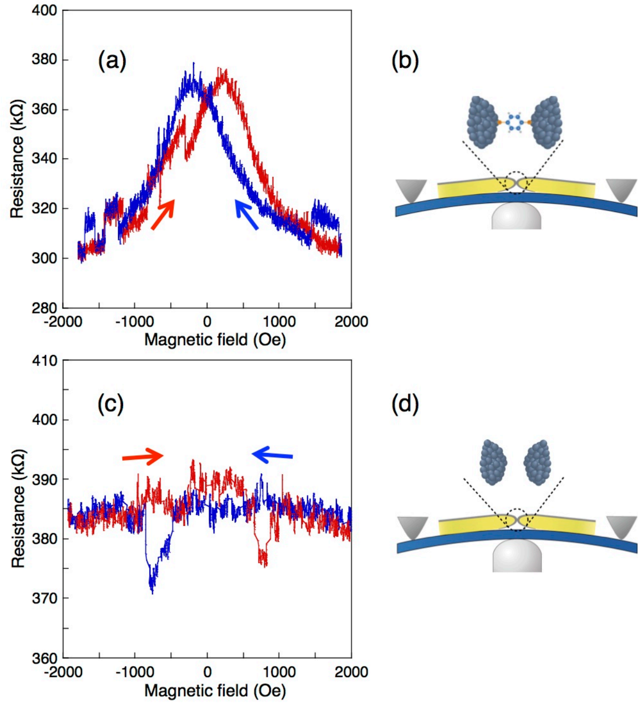

Fig. 4. MR loop for a Ni/BDT/Ni junction (a) and a Ni tunnel junction (c). The molecular and tunnel junctions are illustrated schematically in (b) and (d), respectively.

3. Conclusions

We have studied magnetoresistace in spin-valve devices based on organic thin films, single crystals and single molecules. It was found that the spin-valve characteristics of OMs were strongly affected by film thickness of OMs, and electronic structures between FM electrodes and OMs, which encourages researchers including chemist to design and synthesize novel OMs suitable for spintronic devices.

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