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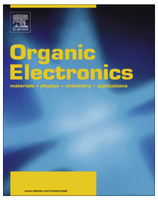

Preparation of lateral spin-valve structure using doped conducting polymer poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)

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ABSTRACT

To perform four-terminal nonlocal spin-valve measurements on organic spin-valves, we fabricated lateral spin-valve devices consisting of doped conducting polymer poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) [PEDOT:PSS] and ferromagnetic $Ni_{80}Fe_{20}$ narrow line (width: 530 nm) electrodes. Although the formula of the nonlocal magnetoresistance with the parameters of doped conducting polymers predicts sufficient nonlocal magnetoresistance, we could not observe any spin signal. The spin diffusion length in the doped PEDOT:PSS device does not appear to be as long as those predicted by both the Elliott–Yafet mechanism and the theory of spin relaxation in organic disordered solids.

1. Introduction

Recently, spintronic applications of organic materials (OMs) have attracted much attention because they are expected to exhibit long spin relaxation times owing to their weak spin–orbit coupling (SOC). A significant number of organic spin-valves (OSVs), in which an organic layer is sandwiched between ferromagnetic electrodes, have been fabricated following a pioneering report on magnetoresistance (MR) in an OSV with tris(8-hydroxyquinolinato)aluminum (Alq_3) [1]. However, the properties of spin transport in OMs remain unclear because all the reported OSVs are two-terminal devices in which the MR of the ferromagnetic electrodes cannot be excluded. To investigate the spin transport, four-terminal nonlocal spin-valve (NLSV) measurements on OSVs have been proposed as performed for conventional metals [2], graphene [3], and doped Si [4].

In NLSV measurements [2], the charge current path is separated from the voltage detection circuit so that the spin accumulation can be detected in lateral spin-valve devices. While sweeping an external magnetic field, the nonlocal voltage depends on the magnetization configuration (parallel or antiparallel) of the neighboring ferromagnetic electrodes. This technique is less sensitive to resistance fluctuations and spurious magnetoresistances, such as anisotropic magnetoresistance (AMR) or Hall effects. It is also convenient to measure the gap distance dependence of the spin signal in the same sample, namely, the spin diffusion length, using additional electrodes. Moreover, the Hanle effect can be measured by rotating the field direction in the same devices so that the spin relaxation time can be estimated from the spin precession. However, such a measurement has not been reported for OSVs.

One of the difficulties in NLSV measurements is the high resistance of OMs. The cross section of the charge current path in a lateral device is much smaller than that in vertical devices. If we assume vertical and lateral devices with typical dimensions of 1 mm × 1 mm × 100 nm and 1 μm × 100 nm × 1 μm, respectively, the difference in resistance is 10^8. Most OMs are therefore not suitable for NLSV measurements because a measurable current cannot be applied to lateral devices. In this sense, two material groups are considered candidates for this method owing to their high

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conductivity. One group comprises molecular conductors including so-called charge transfer complexes, and the other group comprises doped conducting polymers. In addition to the high conductivity in doped conducting polymers, the spin–lattice relaxation times measured by electron spin resonance (ESR) are generally longer than those of molecular conductors and conventional metals. Furthermore, Yu suggested a theory of carrier spin relaxation caused by SOC and polaron hopping in disordered OMs [5,6], because conventional spin relaxation models, such as Elliott–Yafet (EY) and D'yakonov–Perel' (DP) mechanisms, have been developed for crystalline inorganic materials. According to the theory, the spin diffusion length λ_s is $l/4\gamma$ where l and γ denote the mean polaron hopping distance and the SOC measure, respectively. A large λ_s (>1 μm) is expected according to the calculated γ for hole polarons in polymers, indicating that they are potentially suitable for NLSV measurements. In this study, we fabricated lateral devices using poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) [abbreviated to PEDOT:PSS, Clevios$^{\mathrm{TM}}$ PH1000] and performed NLSV measurements. To summarize our results, we could not observe any nonlocal spin signal, and we discuss the reasons for the absence of MR.

2. Experimental

NLSV samples based on the conducting polymer PEDOT:PSS were prepared by electron beam lithography (EBL). A trench with a width of 3 μm was prepared on a resist film on SiO_2 by EBL. After UV/O_3 treatment, an aqueous solution of PEDOT:PSS containing 3 v/v% ethylene glycol (EG) was spin-coated at 3000 rpm for 120 s. Following baking at 135 °C for 20 min, PEDOT:PSS was lifted off in dimethylacetamide to obtain a 40-nm-high PEDOT:PSS line with a width of 3 μm. To ensure high conductivity, the PEDOT:PSS line was additionally immersed in EG for 30 min and annealed at 120 °C for 15 min [7]. The conductivity was approximately 820 S/cm at 300 K and 45 S/cm at 2 K. Subsequently, eight ferromagnetic $Ni_{80}Fe_{20}$ (Py) electrodes with a thickness of 100 nm were patterned on the PEDOT:PSS line by a second EBL process and electron beam deposition. Fig. 1 shows a scanning electron micrograph of a typical sample. The width of the Py electrodes was 530 nm and the smallest gap distance was 420 nm in the measured sample. The neighboring electrodes have different coercive forces because of the pad structures, which weaken the coercive force. This was confirmed from the M–H curves as shown in Fig. 1d. Moreover, we confirmed the existence of nonlocal MR signals in Py/Cu/Py lateral spin-valves prepared with the same deposition setup for Py (not shown).

The measurements were performed in a Physical Property Measurement System (Quantum Design Inc.). The current–voltage (I–V) characteristics were measured with a dc power source (Yokogawa GS210) and a nanovoltmeter (Agilent 34420A) by sweeping the dc bias current up to ±0.18 mA/μm^2. The nonlocal MR was measured by a standard ac lock-in technique by sweeping the magnetic field at a rate of 2 Oe/s.

3. Results and discussion

To observe sufficient nonlocal MR, the conductivity mismatch should be small [8] or a tunneling barrier should exist at the nonmagnetic/ferromagnetic interface. In OSVs, the latter condition is essential because their conductivities are at least a few orders of magnitude less than those of ferromagnetic metal electrodes. In the case of tunneling contact, the change in nonlocal resistance can be described as [2,9]

$$\Delta R = \frac{P^2 \lambda_s}{\sigma A} \exp(-L/\lambda_s) \qquad (1)$$

where P, σ, A, and L denote the effective spin polarization of the ferromagnetic electrodes, the conductivity of the nonmagnetic material, the device area, and the gap spacing, respectively. This formula is valid when $R_i \gtrsim \lambda_s/\sigma A$ where R_i is the barrier resistance [9]. To investigate the electrical properties of the polymer/electrode interface, we measured the I–V characteristics in four-terminal and quasi-four-terminal configurations at room temperature. Fig. 2a shows the results for a sample with a contact area of 2.17 μm^2 and a gap distance of 1500 nm. Although the resistance was almost constant in the four-terminal configuration, it was clearly bias-dependent in the quasi-four-terminal configuration. The resistance-area product was approximately 545 Ω μm^2, implying the presence of an insulating layer probably because of the dopant PSS molecules at the surface. According to X-ray and ultraviolet photoemission spectroscopy on PEDOT:PSS [10,11], the surface is covered by PSS-rich layer and the thickness is estimated to be 35 ± 5 Å. We performed a simulation of I–V characteristics based on elastic tunneling through a rectangular potential barrier which is so-called Simmons' fitting [12], and derived the thickness d and height ϕ of the barrier by fitting with the experimental data (difference between the quasi-four-terminal and four-terminal I–V curves, divided by 2). As shown in Fig. 2b, the obtained parameters by regression analysis using Levenberg–Marquardt method were d = 3.71 nm and ϕ = 0.89 eV, respectively. The thickness of the insulating layer appears to be consistent with the reported values although this is an effective value including the effect of the surface roughness and immersion into EG [7]. The condition $R_i \gtrsim \lambda_s/\sigma A$ is satisfied up to $\lambda_s \sim 2.5$ μm. Although we also prepared Py(100 nm)/SiO_2(2 nm)/PEDOT:PSS samples, the contact resistance and its fluctuation became too large (>1 MΩ μm^2) to allow measurements.

It is known that the charges in various doped conducting polymers are transferred by phonon-assisted variable range hopping (VRH) [13–15]. The four-terminal conductivity in our samples also exhibited semiconducting temperature dependence. Conductivity was plotted on a logarithmic scale against $(T_0/T)^{1/n}$ where n = 1, 2, 4, and T_0 is a constant. The plot for n = 1 is the Arrhenius plot, and those for n = 2 and 4 correspond to quasi-one-dimensional (Q1D) and Q3D VRH fittings, respectively. The best fitting was obtained by the Q3D VRH model with T_0=674 K as shown in Fig. 3a, which can be expressed as $T_0 = 18/k_B\xi^3 N(E_F)$ where $N(E_F)$ and ξdenote the density of