



Research paper

Tunnel magnetoresistance of ferrocene molecules

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ABSTRACT

The spin transport in ferrocene molecules has been examined by using the nonequilibrium Green's function formalism with density functional theory. The ferrocene molecules were sandwiched between the two nickel electrodes in a parallel magnetic configuration, which enhanced the current in comparison with that in an antiparallel spin state and resulting in tunnel magnetoresistance (TMR). The current, having an opposite spin state to that of the ferromagnetic electrode, was the main channel for electron transport. In addition, it became clear that ferrocenylene molecules, having a fulvalene structure with an extended π -conjugation, enhanced the TMR effect.

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1. Introduction

The discovery of giant magnetoresistance (GMR) opened the door to the nanostructuring of magnetic materials and the technological application of spintronics [1–3]. Tunnel magnetoresistance (TMR) is also a magnetoresistance phenomenon and is derived from quantum mechanical tunneling through ferromagnetic layers separated by a thin insulator [4]. TMR can bring about a change in the electrical resistance when the magnetic configuration is parallel or antiparallel. Trilayers of Fe/MgO/Fe show an extremely high TMR effect, allowing the development of magnetic random-access memory technologies and high-frequency oscillators [5,6].

Practical applications of the above spintronic devices require a suitably low bias voltage to induce a high-performance TMR effect within micro-fabricated magnetic devices. Organic materials are emerging materials in the field of spintronics because they have a weak spin-relaxation and a small hyperfine interaction [7]. Furthermore, organic molecular spintronics, in which single molecules are attached to the ferromagnetic electrodes, have also been developed, suggesting a possible roadmap to the post-silicon era [8]. π - and σ -conjugated molecules are possible choices of materials for molecular spintronics because of their relatively low electrical resistance, and scanning tunneling microscopy has been used to explore the molecular TMR effect [9]. In particular, graphene and fullerene compounds have been remarked as a material to induce the tunnel magnetoresistance [10–14].

Recently, theoretical modeling of the electrical conduction in a single-molecule between metal electrodes has been carried out using the nonequilibrium Green's function (NEGF) with density functional theory (DFT) [15–17]. Ferrocene, which has two

π -conjugated cyclopentadienyl (Cp) rings bound to a central iron atom, is one choice for single-molecule electrical conduction because the electrons are delocalized over the whole molecule [18–20]. In particular, one ferrocene molecule exhibits near-perfect conduction through the ferrocene-based molecular wire [21]. In addition, theoretical calculations of related ferrocene-based nanowires suggest the possibility of large spin polarization, resulting in a spin filtering effect [22,23]. In ferrocene, the carbon 2p orbitals are delocalized, forming the π -conjugated system of the Cp ring, which interacts with the central metal 3d orbitals, delocalizing the electrons over the whole molecule. Such delocalized electrons play an important role in inducing spin polarization in molecular devices. In particular, it is predicted that an organic molecule attached to ferromagnetic metals can induce a large spin polarization by the magnetic proximity effect [24]. Therefore, in this study, the current-bias curves of a ferrocene molecule sandwiched between the ferromagnetic nickel electrodes, in which the magnetic configuration is parallel or antiparallel, were calculated. From the calculated results, the mechanism of spin conduction and the possibility of the TMR effect in the ferrocene molecule are discussed.

2. Calculation method

Ferrocene (Fc) and di- and tri-nuclear ferrocene derivatives (Fc2 and Fc3), in which ferrocene molecules are linked directly to each other, were used to analyze the electrical current because the ferrocenylene molecule has an extended π -conjugated system in the central bicyclopentadienylidene (fulvalene) molecule [25]. To combine the ferrocene molecule with a nickel electrode, a thiol group was connected to the cyclopentadienyl ring at the end of the molecule. The chemical structures were optimized by using the

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Gaussian09 package and the B3LYP functional [26] with the LANL2DZ [27] effective core potential (ECP) basis set for the iron atoms and the 6-31G** basis set for all other atoms.

The device structures comprised ferrocene or ferrocenylene molecule sandwiched between two nickel electrodes, in which each electrode consisted of three layers of Ni(1 1 1) with a lateral (4×4) supercell. The semi-infinite left and right electrodes were constructed from the supercell structures. To connect a molecule at the surface of the electrodes, the hydrogen atoms of the thiol groups were removed to form a sulfur-nickel bond with a length of 2.20 Å, as determined from first-principles calculations and reported in the literature [28]. The sulfur atom was placed at the hollow site of the Ni(1 1 1) surface (see Fig. 1).

The electron transport calculations were carried out with the NEGF-DFT formalism using the Atomistix Toolkit (QuantumWise A/S) [29]. In the program, only the valence atomic orbitals are considered in the self-consistent calculation with single- ζ basis sets/polarization functions for iron and nickel and double- ζ basis sets/polarization functions for the other atoms. The basis set functions were defined by the SIESTA code, which included a pseudopotential for the inner shell electrons [30,31]. Additionally, the DFT exchange-correlation was provided by the Perdew–Burke–Ernzerhof functional [32]. A kinetic energy cutoff of 150 Ry was used to perform the DFT calculation. In addition, a 21×21 Monkhorst-Pack \mathbf{k}_{\parallel} (k_a , k_b)-mesh was used for sampling the transverse Brillouin zone. The Landauer–Büttiker formula was adopted for calculating the coherent transport properties between the two nickel electrodes [33]. The calculations were performed for two magnetic configurations, under which the relative orientation of magnetization of the two electrodes was aligned either parallel (PA) or an antiparallel (APA).

The total current (I) can be divided into the partial currents of the spin-up state (I_{\uparrow}) and the spin-down state (I_{\downarrow}). The TMR ratio

is determined from the total current in the PA (I_{PA}) and APA (I_{APA}) magnetic configurations, as follows:

$$\text{TMR} = \frac{I_{PA} - I_{APA}}{I_{APA}}. \quad (1)$$

The currents were calculated at bias voltages (V_b) between 0 and 1.0 V. The transmittance ($T_{\sigma}(E, V_b)$) at an energy level of E under a bias of V_b was also obtained from the calculation. In this study, μ , which is the Fermi level when $V_b = 0$, was determined to be zero. The density of states (DOS) was also obtained from the Green's function.

3. Results and discussion

First, the current–bias characteristics of Fc are plotted in Fig. 2. The total current increased with increasing bias in both magnetic configurations. Fig. 2(a) and (b) also shows the currents divided into the spin-up and spin-down states. Thus, clearly, the nonlinearity of the total current was primarily dependent on the current of the spin-down state, for which the spin direction was the opposite of that of the left electrode. For example, in the parallel configuration, at a bias of 0.20 V, the current of the spin-up state was 1.26 nA, and that of the spin-down state was 2.33 nA. Subsequently, the total currents of the configurations were compared. The difference in the total current is represented by the TMR ratio, calculated by Eq. (1). As shown in Fig. 2(c), the TMR ratio was about 0.12 at a bias of 0.02 V and increased to 0.34 at a bias of 0.21 V. This result suggests that Fc can provide a relatively high TMR at a low bias voltage. Fig. 2(c) also shows the TMR change of polarity around a bias of 0.5 V. The cause of this change will be analyzed as follows using transmission spectra.

The current–bias characteristics mentioned above were also confirmed using transmission spectra. Because transmission tends to depend on \mathbf{k}_{\parallel} , the distribution against \mathbf{k}_{\parallel} should be checked. Hence, the difference in the transmission spectra of the spin states in each magnetic configuration is reflected by the transmission plotted against \mathbf{k}_{\parallel} . Fig. 3(a)–(d) shows the $T(E_f, \mathbf{k}_{\parallel})$ plots of spin-up and spin-down states for each magnetic configuration. The parallel configuration resulted in relatively small values of $T(E_f, \mathbf{k}_{\parallel})$ of the spin-up state (Fig. 3(a)) in comparison with that of the spin-down state (Fig. 3(b)). The same can be said of those of the

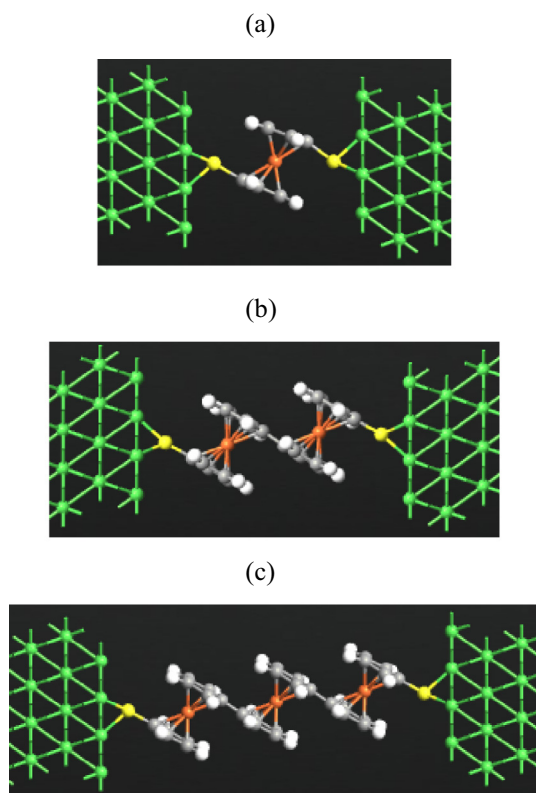


Fig. 1. (a) Fc, (b) Fc2, and (c) Fc3 sandwiched between the nickel electrodes.

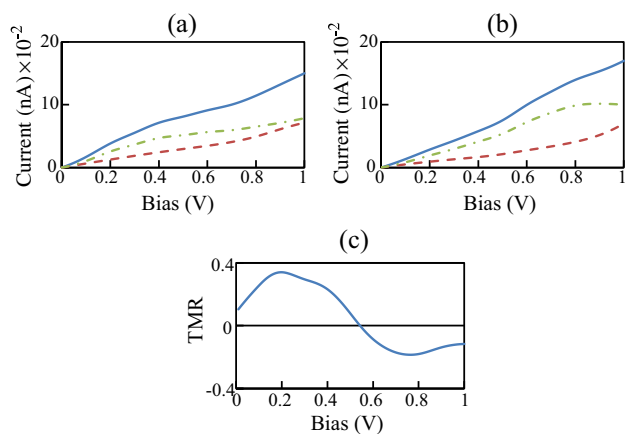


Fig. 2. Current–bias characteristics of Fc in (a) parallel and (b) antiparallel spin configurations. The solid (black), dashed (red), and dot-dashed lines (blue) indicate the total current and the currents of the spin-up and spin-down states, respectively. (c) The plot of TMR ratios versus bias voltages of Fc. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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