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Spin transport in poly(metalarenylsilane)

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We focused on the spin transport properties of polymers containing ferrocene and the related transition-metal-benzene sandwich compound (metal = Cr and V) with a silicon bridge such as poly(ferrocenylsilane) and poly(metalarenylsilane). As a model system, a sulfur-substituted oligomer was put on gold electrodes via the sulfur-gold interaction. Spin transport between the two gold electrodes was calculated using a non-equilibrium Green's function formalism and density functional theory. We have found that the oligomer containing Cr or V atoms exhibited an almost perfect spin filter behavior in which all the $3d_z^2$ orbitals contributed to the electron transport. © 2012 American Institute of Physics. [doi:10.1063/1.3680590]

Since ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$) can repeat oxidation and reduction in stability, ferrocene-containing polymers have been studied extensively as functional electronic materials.¹ Manners and coworkers have developed poly(ferrocenylsilane), which is a macromolecule of ferrocene with silicon bridges, as shown in Figure 1(a) ($m = 0$, $M = \text{Fe}$).² Electronically delocalized materials were realized using p-type doping of the polymers. Also, polymers containing transition-metal atoms other than iron have also been studied extensively. Poly(chromarenylsilane), which is composed of Cr-Bz sandwich compounds with silicon bridge as shown in Figure 1(a) ($m = 1$, $M = \text{Cr}$), was prepared.³ Poly(vanadoarenylsilane), which contains V-Bz sandwich compounds with silicon bridge, had the spin-active metal centers in the main chain.⁴ These materials are promising candidates for spintronics applications.

Recent theoretical studies have developed a first-principle non-equilibrium Green's function (NEGF) formalism with density functional theory (DFT).^{5,6} Transport properties of poly(ferrocenylsilane) and the related ferrocene polymers have been comparatively studied.^{7,8} The transport properties are dependent on the bridge group species. Multi-decker complexes containing transition-metal atoms (V, Fe, Ni) and cyclopentadienyl (Cp) rings or benzene (Bz) rings also have attracted attention as a spin-filter material.⁹ In particular, the Bz-vanadium complex is expected to realize a one-dimensional half-metallic ferromagnet.¹⁰

Manners showed the existence of strong metal-metal interactions via silicon, which was more polarizable than carbon, in poly(ferrocenylsilane)s from cyclic voltammetry studies.¹¹ Therefore, we also expected a peculiar spin behavior in poly(metalarenylsilane)s. In this study, we investigated the spin transport properties in poly(ferrocenylsilane) and poly(metalarenylsilane) (metal: Cr and V), which have been synthesized, and focused on the relationship between molecular structure and spin filter behavior. We have also examined the band structures of the polymers.

The band structure and spin transport were calculated using the Atomistix Toolkit,¹² which is based on the DFT-

based SIESTA code, because it was necessary to calculate the wide electronic structures using the first-principle method without system-dependent parameters.^{13,14} We employed the local spin density approximation (LSDA)

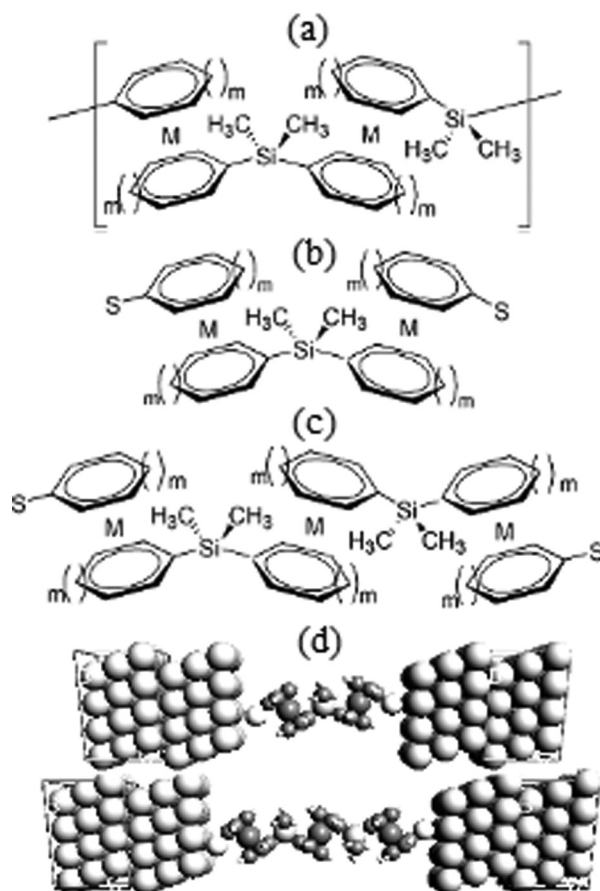


FIG. 1. Chemical structures of (a) polymer, (b) dimer, and (c) trimer of Fe ($m = 0$), Cr, and V ($m = 1$). (d) Configuration of the oligomer between the two gold electrodes. We constructed a scattering region that included the oligomer (molecular region) and the three gold layers with a lateral (4×4) supercell as part of the electrodes. The default value of 2.88 \AA in the program package was chosen as the bond length of the Au–Au bond of the face-centered cubic Au crystal. The oligomers were attached to the left and right Au(111) surfaces of the three gold layers.

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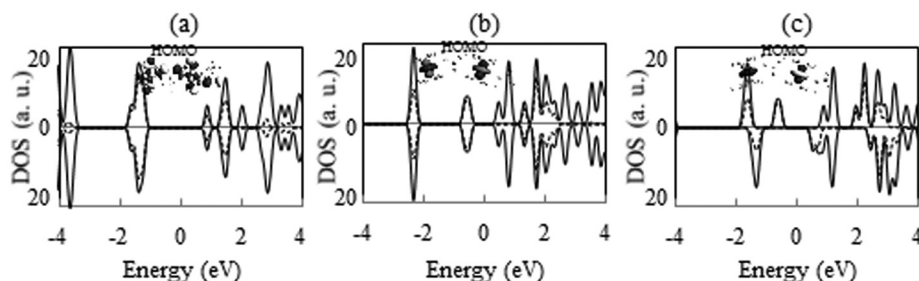


FIG. 2. DOS plots of polymers of (a) Fe, (b) Cr, and (c) V, which were calculated from the band structures. The straight line and the dotted line indicate the total DOS and the PDOS for 3d orbitals of the transition-metal atoms. The upper panel of the plot is for the spin-up states and the lower panel is for the spin-down states.

pseudo-potential for exchange correlation with a double- ζ plus polarization basis set for all the atoms. The mesh cut-off was set at 75 Ry in the calculation. Geometry optimization was carried out using conjugate gradient relaxation until the forces were smaller than 0.01 eV \AA^{-1} .

Figure 1(a) shows a unit cell of the polymer structure, labeled as M-polymers ($M = \text{Fe, Cr, and V}$). In order to calculate the electron transport properties of the polymers, we constructed finite structural models, i.e., oligomers. Figures 1(b) and 1(c) show the configuration of sulfur-substituted oligomers, which are used to construct a model of an oligomer between two gold electrodes via the S-Au interaction, as shown in Figure 1(d). A sulfur atom was placed on the hollow site of the Au(111) surface with S-Au distances of $2.37\text{--}2.39 \text{ \AA}$.¹⁵ We labeled the complexes as M-dimer (Figure 1(b)) and M-trimer (Figure 1(c)) ($M = \text{Fe, Cr, and V}$). In the above models, the coordinates of the gold atoms in the molecular region are fixed, whereas those of the other atoms are fully optimized.

Electron transport calculations were performed using the NEGF formalism with the DFT approach.¹⁶ Here, we considered the zero-bias limit and no spin-flip scattering. The transmittance ($T(E)$) was calculated from the coupling strength introduced by the self-energies of the electrodes and the retarded/advanced Green's function of the molecular region.

Spin filter efficiency (SFE) was calculated as follows:

$$\text{SFE} = \frac{[T_{\text{up}}(E_F) - T_{\text{down}}(E_F)]}{[T_{\text{up}}(E_F) + T_{\text{down}}(E_F)]} \times 100\%, \quad (1)$$

where $T_{\text{up}}(E_F)$ and $T_{\text{down}}(E_F)$ were the transmission of spin-up and spin-down states at the Fermi level, respectively.

First, we investigated the optimized structures and the band structures of the polymers. The optimized structure of the Fe-polymer coincided well with the experimental and calculated results of Fe-oligomers in Refs. 2 and 7. However, since the Cr- and V- oligomers have not yet been isolated, we could not compare our results with experiment. Figures 2(a)–2(c) indicate the density of states (DOS) calculated from the band structures of the Fe-, Cr-, and V-polymers. In the DOS plots, the Fermi level is located at 0 eV. The Fe- and Cr-polymers had a symmetric total DOS (TDOS) plot of the spin-up and spin-down states and exhibited semiconducting properties. The projected DOS (PDOS) suggests that the valence and conduction bands consisted of metal 3d orbitals. In particular, we found that the HOMO of the Fe-polymer is formed by the Fe $3d_{xy}$ orbital and the Cp π orbitals. The HOMO of the Cr-polymer consisted of the Cr $3d_z^2$ orbital.

Each HOMO has a small contribution from the silicon bridges.

Unlike the Fe- and Cr-polymers, the V-polymer had an asymmetric DOS for spin-up and spin-down states. As shown in Table I, the Mulliken population of a unit cell in the V polymer had approximately two spin-up states and one spin-down state due to the odd numbers of 3d electrons in one V atom. The PDOS in Figure 2(c) also suggests that the origin of asymmetry is caused by 3d electrons. Furthermore, the HOMO is formed from $3d_z^2$ orbitals of the V atom with no contribution from the silicon bridge. Our calculated results coincided well with the paramagnetic properties of poly(vanadoarenylsilane) observed by ESR measurements, which indicated that the spins were located at the V atoms.⁴ The band structure of the polymers of Fe, Cr, and V suggests that the silicon bridge does not permit delocalization of π electrons of the Cp or the Bz ring between the unit cells, which was also discussed in Ref. 8.

Next, we consider electron transport in the dimer between the gold electrodes. Table I shows the calculated results for conductance and SFE. The Fe-dimer exhibited very low conductance with no spin filter behavior. In contrast, the Cr- and V-dimers had a high conductance with an almost perfect SFE. These results are clarified by the transmission spectra in Figures 3(a)–3(c). The Fe-dimer had a symmetric transmission spectrum of spin-up and spin-down states with no transmission at the Fermi level. The Cr- and V-dimers had an asymmetric transmission spectrum with a finite transmission at the Fermi level. As shown in Figures 3(a)–3(c), we also examined the molecular-projected self-consistent Hamiltonian (MPSH). The HOMO of the Fe-

TABLE I. The Mulliken population of the polymer, dimmers, and trimers of Fe, Cr, and V.

Oligomers		M1 ^a		M2 ^a		M3 ^a	
		Up	Down	Up	Down	Up	Down
Polymer	Fe	3.10	3.10	3.12	3.12	-	-
	Cr	1.99	1.99	1.99	1.99	-	-
	V	2.07	0.93	2.07	0.93	-	-
Dimer	Fe	3.03	3.03	3.04	3.04	-	-
	Cr	2.06	1.83	2.14	1.78	-	-
	V	2.00	0.96	2.01	0.98	-	-
Trimer	Fe	3.04	3.04	3.04	3.04	3.04	3.04
	Cr	2.07	1.87	2.14	1.79	2.12	1.78
	V	1.99	0.98	2.00	0.98	1.99	0.98

^aM1, M2, and M3 indicate the transition-metal atoms located from left electrode.

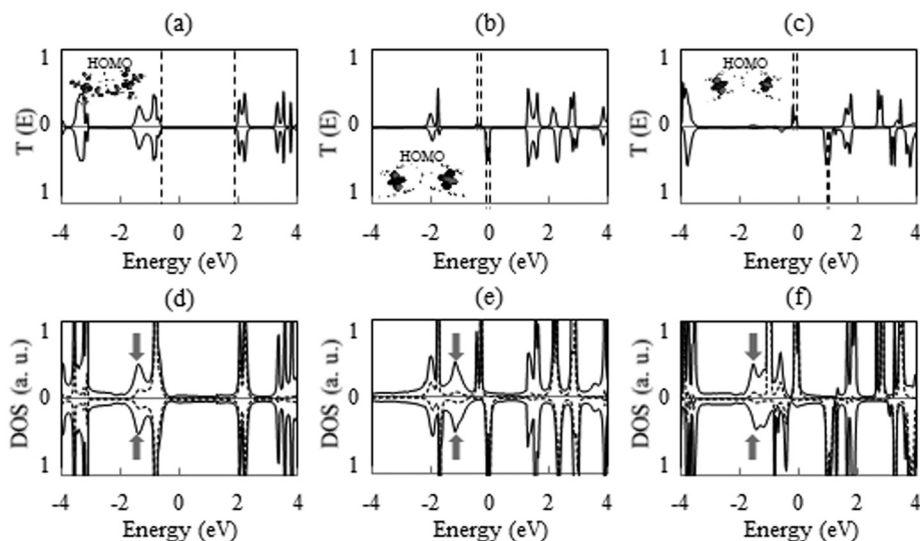


FIG. 3. Transmission spectra of dimers of (a) Fe, (b) Cr, and (c) V between two gold electrodes. The dotted lines indicate the energy levels of the MPSH around the Fermi level. DOS for dimers of (d) Fe, (e) Cr, and (f) V between two gold electrodes. The straight line and the dotted line indicate the total DOS and the PDOS for 3d orbitals of the transition-metal atoms. The peaks in the TDOS indicated by the arrow primarily depend on S atoms. The upper panel of the plot is for the spin-up states and the lower panel is for the spin-down states.

TABLE II. The conductance and SFE of the dimers and trimers of Fe, Cr, and V between the two gold electrodes.

Oligomers		Conductance (μS)	SFE
Dimer	Fe	7.23×10^{-3}	0.00
	Cr	16.5	1.00
	V	2.27	1.00
Trimer	Fe	3.30×10^{-3}	0.00
	Cr	15.9	1.00
	V	2.10	1.00

dimer contains an Fe $3d_{xy}$ orbital and Cp π orbitals in two Fe atoms. However, the HOMO is located below the Fermi level and has a small contribution to electrical conduction. In contrast, the energy levels of the MPSH in Figures 3(b) and 3(c) suggested that the HOMO of the Cr- and V-dimers is formed by $3d_z^2$ orbitals, which raises the transmission.

The origin of transmission at the Fermi level was examined using the DOS of the dimers in more detail. The transmission spectra of the dimers were strongly dependent on the TDOS. In particular, as described in Figures 3(e) and 3(f), the 3d electrons of Cr or V atoms caused an asymmetry of the transmission spectra at the Fermi level. As described in Figure 2(b), the Cr-polymer had a symmetric TDOS of the spin-up and spin-down states. Therefore, the 3d orbitals of Cr atom were influenced by adhesion of the Cr-dimer to the gold surface.

There was a difference in electronic states between the Cr- and V-dimers. From Figures 3(b) and 3(c), we inferred that the spin transport in the Cr-dimer depended on the spin-down states at the Fermi level, and the V-dimer spin-up states

contributed to transport. This difference arises because the Cr atom has one more electron than the V atom. The Mulliken population of the Cr- and V-dimers could be understood from the difference in their electronic states. As shown in Table I, adhesion of the Cr-dimer to the gold electrodes resulted in a small difference in the numbers of spin-up and spin-down states on the two Cr atoms. In contrast, the V-dimer had approximately two spin-up states and one spin-down state on each V atom, similar to the V polymer. Using the Mulliken population results, we found that spin transport strongly depended on the energy levels of the MPSH states, regardless of whether there was spin polarization in the molecules or not.

Although the Cr-dimer had a closed-shell system similar to the Fe-dimer, only the Cr-dimer showed spin-filtering activity. It is assumed that substitution with sulfur, which has energy levels around -1.75 eV (Figures 3(d)–3(f)), leads to perturb the HOMO of the polymers. In particular, because the Cr-polymer has the HOMO formed by only Cr $3d_z^2$ orbitals, sulfur-substitution may enhance the interaction between the neighboring Cr $3d_z^2$ orbitals via polarizable silicon, resulting in the splitting of the energy levels.

Finally, we checked the influence of molecular length on electron transport in the scattering region. Table II shows the conductance and SFE of Fe-, Cr-, and V-trimers. Adding one more ferrocene or metal-arene unit to the trimer lowered the conductance. However, the spin filter behavior of the trimers did not change compared to that of the dimers. The Fe-trimer also had a zero value of SFE with a low conductance because the transmission at the Fermi level was almost zero. The HOMO (-0.5 eV) formed

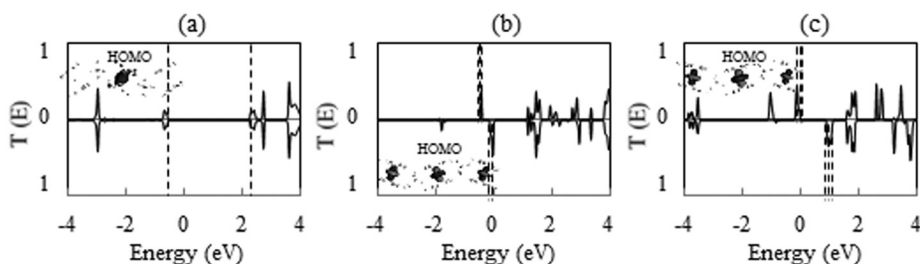


FIG. 4. Transmission spectra of trimers of (a) Fe, (b) Cr, and (c) V between two gold electrodes. The dotted lines indicate the energy levels of the MPSH around the Fermi level. The upper panel of the plot is for the spin-up states and the lower panel is for the spin-down states.

by the $3d_{xy}$ orbital on the central Fe atom also resulted in a low conductance. In contrast to the Fe-trimer, the SFE values suggested that the Cr- and V-trimers exhibited perfect spin filter behavior. The HOMO, formed by $3d_z^2$ orbitals of all the transition-metal atoms, increased the conductance of the trimers.

Similar to the results for dimers, the Mulliken population suggested important differences between Cr- and V-trimers. Table I shows that the Cr-trimer had a certain population difference between spin-up and spin-down states. The V-trimer had approximately two spin-up states and one spin-down state on the three V atoms. The Cr- and V-dimers showed the same tendency. For the trimers, spin transport depended on the MPSH states of the 3d orbitals at the Fermi level, regardless of the difference in spin polarization in the molecules (Fig. 4).

In summary, the Cr and V oligomers had a high conductance with perfect spin filter behavior. Comparing DOS and transmission plots with the Mulliken population of transition-metal atoms, we found that the spin transport behavior strongly depended on the MPSH states at the Fermi level, regardless of the difference in spin-up and spin-down states. Although high performance spin filter behavior could be expected from our results, poly(chromarenylsilane) and poly(vanadoarenylsilane) have been shown to be air-sensitive.^{3,4} If researchers could surmount this difficulty, these

polymers would become the promising candidates for spin filter devices.

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