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Electrical control of spin polarization of conductance in Mn-encapsulated Si nanotube

Yan-Dong Guo[1,2], Xiao-Hong Yan[1,2*], and Yang Xiao[2]

[1]College of Electronic Science and Engineering, Nanjing University of Posts and Telecommunications, Nanjing 210046, China
[2]College of Science, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China

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Compared with the use of magnetic methods, electrical manipulation of the spin polarization of a current could greatly reduce the devices' dimensions and energy consumption. Using first-principles calculations, the spin-dependent electronic transport of a Mn-encapsulated Si nanotube contacted with Cu electrodes is investigated. As the gate voltage decreases, the conductance changes from spin unpolarized to spin polarized (the polarization could reach 90%). Electron transfer between Si and Mn atoms modulated by the gate voltage is found to be the physical mechanism. Because Si and Cu are fundamental materials in integrated circuits, these findings may be quite useful for developing Si-based spintronic devices.

Spintronics is a promising candidate for future nanoelectronics applications.[1–3] Silicon is the fundamental material in the semiconductor industry, so Si-based spintronics has become a focus of intensive research.[4] However, sp^2 hybridization is not favorable in silicon. Thus, Si nanotubes that are hollow inside, like carbon nanotubes, are hard to form.[5,6] Metal encapsulation can reportedly stabilize Si cage clusters,[5,7,8] and Si nanotubes could form by their assembly.[9–12] The stability of such tubes has been proven by theoretical studies,[13] and the corresponding nanotube bundles have been synthesized experimentally through epitaxial self-assembly.[14,15] Because of the presence of d orbitals, 3d transition metal-encapsulated tubes exhibit various interesting magnetic properties,[10,12,16] showing great application potential. In this study, we focus on the Mn-doped Si nanotube and propose a three-terminal device contacted with Cu electrodes. We found that the current of the system could be electrically modulated from from spin unpolarized to spin polarized by varying the gate voltage V_g. Further analysis shows that the electron transfer between Si and Mn atoms modulated by V_g is the underlying physical mechanism. For spintronics, controlling the spin polarization of a current is a key point. Compared with the use of magnetic methods, electrical manipulation of the spin polarization of a current could greatly reduce the devices' dimensions and energy consumption.[17–19] Because Si and Cu are currently the fundamental materials in integrated circuits, these findings might be quite useful for the development of Si-based spintronic devices.

To explore the transport properties, we performed first-principles calculations based on a combination of density functional theory and the nonequilibrium Green's function (NEGF). The calculations were made using the Atomistix Toolkit package.[20,21] The mesh cutoff energy was set to 150 Ry, with a $1 \times 1 \times 50$ k-point mesh in the Monkhorst–Pack scheme.[22] The Perdew–Burke–Ernzerhof formulation of the generalized gradient approximation was chosen for the exchange–correlation function.[23] We used the double-zeta basis set as the local numerical orbitals and checked the accuracy by comparison with former studies.[24] To prevent interactions with adjacent images, a supercell with sufficient vacuum space (more than 10 Å) was employed. The nanotube was fully optimized until all the forces were less than 0.02 eV/Å.

In the NEGF scheme, the current of a system is calculated through the Landauer–Büttiker formula

$$I(V_b, V_g)_{\uparrow\downarrow} = \frac{2e}{h}\int T(E, V_b, V_g)_{\uparrow\downarrow}[f(E-\mu_L) - f(E-\mu_R)]\,dE,$$

where $\mu_{L/R}$ and $f(E-\mu_{L/R})$ are the chemical potential and Fermi function of the left (or right) electrode, respectively. $V_b = (\mu_L - \mu_R)/e$ is the bias window. A gate voltage V_g is introduced by adding an external electrostatic potential to the effective potential $V^{\mathrm{eff}}[n](\mathbf{r})$ in the one-electron Kohn–Sham Hamiltonian. This is done by shifting the diagonal terms of the Hamiltonian H by $-eV_g$ (only for the scattering region of H, which is influenced by the gate electrode). For systems with metallic electrodes, this is a reasonable approximation.[20,25]

$$H = -\frac{\hbar}{2m}\nabla^2 + V^{\mathrm{eff}}[n](\mathbf{r}).$$

$T(E, V_b, V_g)_{\uparrow\downarrow}$ is the transmission probability for an electron with up (or down) spin to transit the system, and it is obtained (omitting the denotations of the spin, V_b, and V_g) according to

$$T(E) = \mathrm{Tr}[\Gamma_L(E)G^R(E)\Gamma_R(E)G^A(E)],$$

where $G^{R/A}$ is the retarded (or advanced) Green's function, and $\Gamma_{L/R}$ is the coupling matrix between the scattering region and the left (or right) electrode. In this work, we confine our studies to the zero-bias ($V_b = 0$) condition, which dominates the transport properties of a system under low bias.

Previous studies showed that an infinite Mn-doped Si nanotube is conducting and that near the Fermi energy in the minority spin there is an energy gap.[10] It is predicted that moving the gap to the Fermi level would make the tube exhibit half-metallicity.[10] As is well known, in three-terminal devices, the orbital energies of the scattering region can be shifted by V_g; i.e., a positive (or negative) V_g would lower (or raise) the energy. This effect has been observed in practical single-molecular devices.[26] Thus, integrating the tube into a three-terminal device is a possible method of modifying its transport properties. However, the band gap mentioned above is observed in an infinite nanotube.[10] For integration into a device, it has to be cut into a finite one and contacted with metallic electrodes (Fig. 1). However, this procedure may strongly affect the electronic properties of the tube. Thus, it is necessary to investigate its performance within a realistic device environment.

Considering the calculation cost, a finite nanotube of $Si_{30}Mn_4$ (Fig. 1) is adopted to study the transport properties.

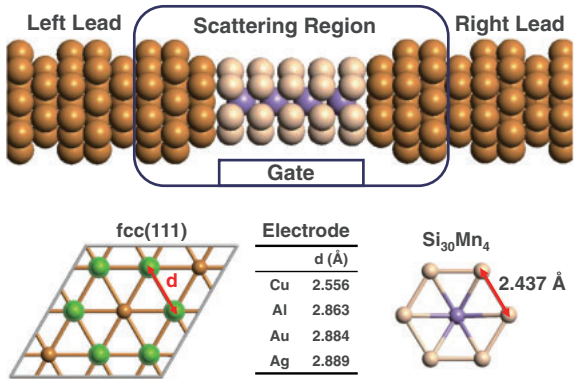

Fig. 1. Geometric view of the Cu–$Si_{30}Mn_4$–Cu system and the structural parameters for the bulk metals (Cu, Al, Au, and Ag) and nanotube $Si_{30}Mn_4$.

Au, Ag, Cu, and Al are commonly used electrode materials. Among these four fcc metals, the (111) surface of Cu matches the best with that of the Si nanotube's cross section (see the lower panel of Fig. 1). Moreover, Cu is a fundamental material in integrated circuits. Thus, we choose Cu nanowire for the electrodes and used the (111) surface as the contact surface. The distance between the electrode and nanotube is set to 2.35 Å, which is obtained by minimizing the total energy of the entire system. The setup of the entire three-terminal device is shown in Fig. 1. As mentioned above, the gate voltage is induced by adding an external electrostatic potential to the effective potential $V^{\text{eff}}[n](\mathbf{r})$.

Because the electronic transport is determined mainly by the transmission at the Fermi energy, we focus on the conductance at E_F. Before a gate voltage is introduced, at the Fermi level, the conductance of the system is spin polarized, and the up-spin conductance is higher than the down-spin one [Fig. 2(a), $V_g = 0$]. We here define the spin polarization of the conductance as $(G_{up} - G_{down})/(G_{up} + G_{down})$. For our Cu–$Si_{30}Mn_4$–Cu system, this value is about 50% at E_F [Fig. 2(b)]. That is, if a small finite bias voltage is applied, the current will be 50% spin polarized.

To modulate the spin polarization, we introduce the gate voltage. Figures 2(a) and 2(b) show the spin-dependent conductance and the corresponding spin polarization under a series of V_g values. When a positive V_g is applied, the up-spin conductance decreases monotonously with increasing V_g [Fig. 2(a)]. In contrast, the down-spin conductance increases monotonously [Fig. 2(a)]. The up- and down-spin conductances tend to converge. Correspondingly, the spin polarization of the conductance decreases as V_g increases [Fig. 2(b)]. Surprisingly, when V_g increases to 9 V, the up- and down-spin conductances are almost the same. Consequently, the spin polarization of the conductance becomes nearly zero; i.e., the current produced by the device is spin unpolarized when $V_g = 9$ V.

We next apply a negative V_g. The down-spin conductance decreases gradually as V_g decreases from 0 V and finally goes to almost zero when $V_g \leq -4$ V. In contrast, the change in the up-spin conductance is somewhat complicated. When V_g decreases from 0 to -2 V, the up-spin conductance remains unchanged. In the range of $-2 \leq V_g \leq 0$ V, the spin polarization continues to increase because of the decrease in the down-spin conductance. However, when V_g decreases further, the up-spin conductance declines rapidly. At $V_g = -6$ V,

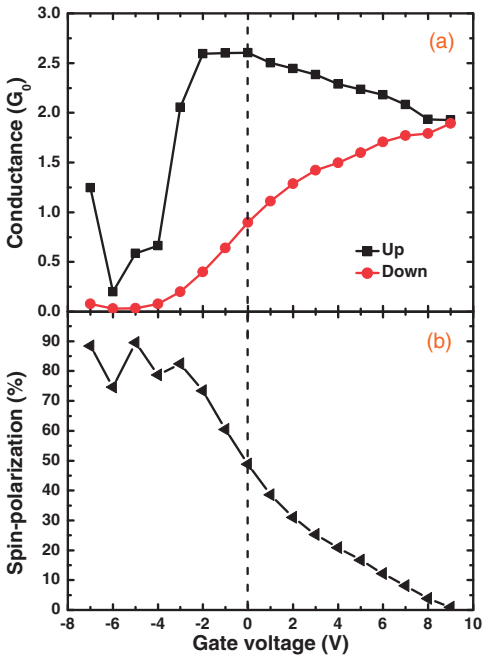

Fig. 2. (a) Spin-dependent zero-bias conductance varies with the gate voltage for the Cu–$Si_{30}Mn_4$–Cu system. G_0 is the conductance quantum ($G_0 = 2e^2/h$). (b) Corresponding spin polarization of the conductance.

it goes to a minimum value and then increases again. This abnormal behavior makes the spin polarization oscillate in the range of $-7 \leq V_g \leq -3$ V [Fig. 2(b)]. Although oscillation appears, the spin polarization remains above 0.75 and even increases to 0.90. For practical application, the oscillation could be avoided by restricting the working voltage of V_g to $[-3, 9]$ V. Within this range, the spin polarization of the conductance would vary gradually. As a result, it becomes possible not only to produce a current with high spin polarization, but also to realize a current with any ratio of up-spin to down-spin electrons in a large range. Most importantly, the modulation is realized using an electrical method (V_g). Compared with the use of conventional magnetic means, this would reduce the dimensions and energy consumption of devices. Si and Cu are the fundamental materials in the semiconductor industry; thus, we believe our results would be quite useful for the application of spintronics in Si-based structures.

In conventional three-terminal devices, the orbital energies and corresponding electronic transmissions could be shifted by V_g.[26] To see the energy shift effect in our system, we plot the spin-dependent transmission spectra under different V_g, as shown in Fig. 3. From Figs. 3(a) to 3(e), V_g increases from -3 to 9 V. According to the shifting mechanism, the transmission spectra should shift down the energy axis from Figs. 3(a) to 3(e). However, the spectra do not change at all. We pick up three typical inflection points, α, β, and γ. These points do not move from Figs. 3(a) to 3(e), except for a very small shift of α at $V_g = 3$ and 9 V. Obviously, in such a system, the energy shifts of the transmission spectra are insensitive to V_g. On the other hand, when V_g increases, the difference between the up- and down-spin transmission around E_F becomes smaller [Figs. 3(a) to 3(e)]. There must be some other reasons for the V_g-induced variation in the spin polarization.

In a previous study, Kong et al.[24] found that the encapsulation of metal atoms not only stabilizes the structure of the

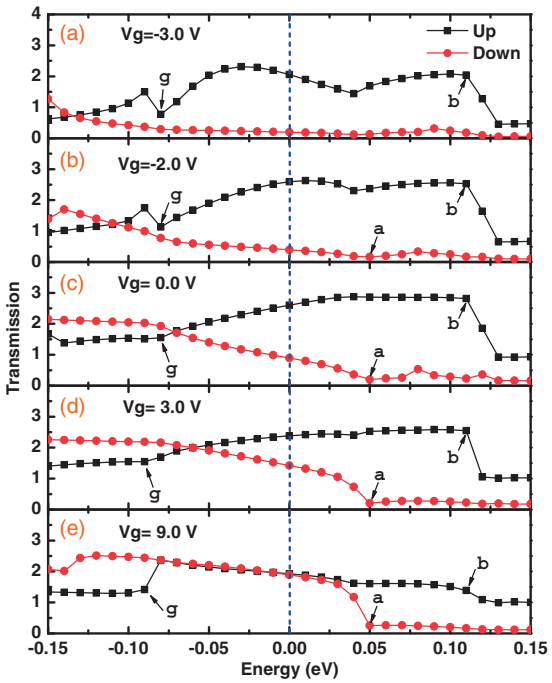

Fig. 3. Spin-dependent zero-bias transmission spectra for Cu–$Si_{30}Mn_4$–Cu under different gate voltages. Zero energy is set to the Fermi level.

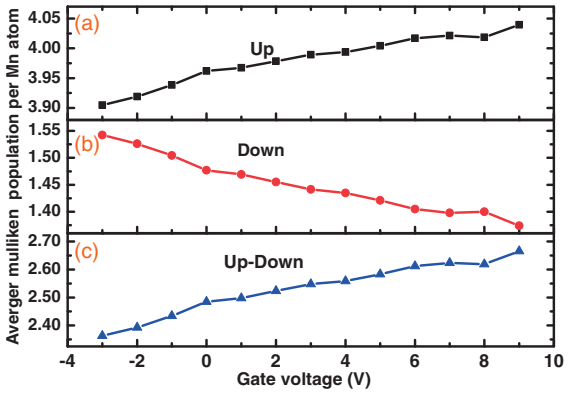

Fig. 4. Average Mulliken population per Mn atom versus the gate voltage for V_g in the range of $[-3, 9]$ V for Cu–$Si_{30}Mn_4$–Cu system. (a) Up spin, (b) down spin, and (c) their difference (up − down).

Si nanotube, but also decreases its conductance because the electrons will be transferred from the sp orbitals of Si to the d orbital of the metal. As is well known, d electrons are more localized than s or p electrons. If charge transfer exists in our system, it may be the underlying mechanism, as the phenomenon of electron transfer modulated by V_g has been reported.[27,28]

For our system, the spin-dependent average Mulliken population per Mn atom versus V_g is plotted in Fig. 4. We here focus on the V_g range of $[-3, 9]$ V because in this range the spin polarization exhibits a smooth monotonic change, and the mechanism will appear more obviously. As we can see, the up-spin Mulliken population of Mn becomes high when V_g increases [Fig. 4(a)]. In contrast, the down-spin population decreases when V_g increases [Fig. 4(b)]. For electron transfer between Si and metal atoms, an increase in the Mn population indicates a decrease in the electrons on Si, and a decrease in the Mn population indicates an increase

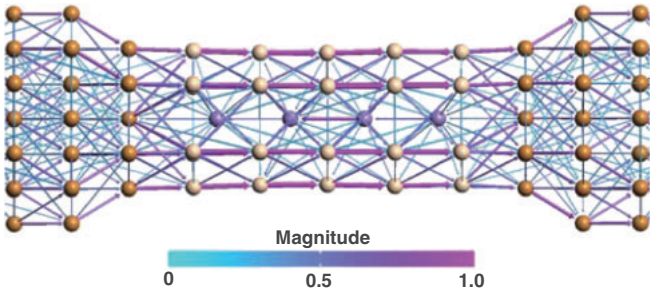

Fig. 5. Transmission pathways of up-spin electrons in the scattering region of Cu–$Si_{30}Mn_4$–Cu system at the Fermi level under zero bias. The transmission pathway contributions come from the left electrode. Further, the magnitude is illustrated by both the size and color of the arrow, which points in the transmission direction. The values were normalized by the largest one. To show the pathways clearly, the bonds between atoms are not shown.

in the electrons on Si. Figure 4(c) shows that the difference in the Mulliken population between up and down spins varies monotonously with V_g. Previous studies showed that in metal-doped Si nanotube systems, transmission occurs mainly through Si atoms.[24] Thus, the increase (decrease) in the electrons on Si will induce an increase (decrease) in the conductance. Thus, for our system, when V_g becomes high, the increase in the up-spin population on Mn will cause the up-spin conductance to decrease. For the down spin, the inverse occurs. As a result, the spin polarization varies monotonously with V_g [Fig. 2(b)]. Note that this modulation is based on the intrinsic transport of the Cu–$Si_{30}Mn_4$–Cu system. Before V_g is introduced, the spin polarization of the transmission is about 0.5 (Fig. 2, $V_g = 0$), which is the starting point for the modulation. In brief, the variation in the spin polarization is not induced by the shifting of the transmission spectra but is caused by electron transfer between Si and Mn atoms, which is modulated by V_g.

We take the up-spin case as an example to show that the electrons are indeed transmitted mainly through the orbitals of the Si atoms. Figure 5 plots the transmission pathways of up-spin electrons in the scattering region at the Fermi level. It could help us observe the electronic transmission in real space, where the magnitude of the transmission is illustrated by both the size and color of the arrow. Apparently, the transmission occurs mainly at the outer layer where the Si atoms are located. In the inner region, where the Mn atoms are located, the transmission is quite small. The transfer of electrons from Mn to Si (or from Si to Mn) would increase (or decrease) the conductance of the system. A similar phenomenon has also been observed in the down-spin case, which is not shown.

In a realistic system, the gate electrode will be constructed from metallic materials and isolated from the scattering region by a dielectric layer. The gate electrode will affect the scattering region through the emitted electric field. In this work, we simulated this field-induced effect, although the actual gate electrode's structure is not involved in our calculation. The gate electrode provides an external potential localized in the scattering region, which modifies the electronic structure of this region. Because of the particular structure of the Si nanotube (the outer atoms are Si, and the inner atoms are Mn), charge transfer occurs between the sp orbitals of Si and the d orbitals of Mn. This transfer is found

to be modulated by the gate voltage but occurs in opposite directions for up and down spins. Because the electronic transport capacities of the sp and d orbitals differ (d orbitals are more localized than sp orbitals), the up- and down-spin conductances also occur in opposite directions, changing the spin polarization. In short, the gate voltage could control the spin polarization of the device's output current. Note that here we investigate only an ideal case. For the practical application of such a device, more work is necessary because its performance might be influenced by various factors, such as defects, the tube length, and the electrode–tube contact geometry.

In summary, through first-principles calculations, the spin-dependent electronic transport of the finite nanotube $Si_{30}Mn_4$ contacted with Cu electrodes is investigated. We demonstrated that the spin polarization of the transmission could be modulated by V_g from 0 to 90%, i.e., from the spin-unpolarized to almost completely spin-polarized states. Through Mulliken population analysis, the electron transfer between Si and Mn atoms modulated by V_g is found to be the physical mechanism, not the conventional V_g-induced energy shift. Electrically controlling the spin polarization of a current is quite useful for designing and applying nanodevices and decreasing their energy consumption. Moreover, Cu and Si are currently the fundamental materials in integrated circuits, so we believe our findings would be very useful for the development of Si-based spintronic devices.

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