Effect of gating on the transport properties of a Si$_4$ cluster

Z. X. Dai, X. Q. Shi, X. H. Zheng, and Z. Zeng*

Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences and Graduate School of the Chinese Academy of Sciences, Hefei 230031, People’s Republic of China

(Received 29 September 2005; published 12 January 2006)

The effect of gate voltage on the transport properties of Si$_4$ cluster coupled with two atomic scale Al(100) electrodes has been investigated using a recently developed ab initio nonequilibrium Green’s function technique. Motivated by a recent experiment [Champagne et al. Nano Lett. 5, 305 (2005)], the gating effect is probed in three cases with different contact distances. The equilibrium conductance is found to oscillate with the gate potential for all contact distances. We elucidate that this oscillatory behavior is very closely related to the variation of the system density of state at Fermi level. Moreover, we also demonstrate that the charge transfer is not the key factor to determine such a conductance oscillatory behavior. Through the analysis of the eigenchannel decomposition of the conductance, we suggest that gating does not change the eigenchannel number, and that the appearance of the conductance maximum results from the saturation of one or two eigenchannels. Even with the modification of gating, Si$_4$ cluster still exhibits a negative differential resistance behavior. In particular, it also displays a negative transconductance behavior for a small fixed drain bias.

DOI: 10.1103/PhysRevB.73.045411 PACS number(s): 73.63.−b, 85.65.+h, 36.40.−c

I. INTRODUCTION

During the past decades, electron transport through atomic scale conductors such as molecules or clusters, viewed as the possible components of future molecular electronic devices, has become a very active research area both experimentally and theoretically. In all these studies, the investigated molecular devices can mainly be divided into two kinds: two-terminal and three-terminal devices. Two-terminal systems are often sandwiched structures, in which atomic scale conductors couple with two metallic electrodes. To control the transport through the two-terminal devices and realize single-molecule-based transistors, three-terminal devices are frequently adopted, in which an additional gate terminal is applied near the molecules or clusters in the two-terminal devices.

Since such three-terminal devices could be ultimately the desired devices for the applications of molecules in electronics, for example, an alternative to a metal-oxide-semiconductor transistor, they have attracted intensive interests. Theoretically, Taylor et al. probed a C$_{60}$ three-terminal molecular device and found that a gate potential can inhibit charge transfer and thus induce a conductance gap near the Fermi level. Liu studied a Ti-contacted single-walled carbon nanotube (SWNT) and presented that gate voltages dramatically affect the transport properties of a SWNT. Ventra et al. have also calculated the transport through a benzene-1, 4-dithiolate molecule with a gate terminal. They observed that an external gate field can significantly change the resistance of the molecule and that the source-drain current can be changed by more than one order of magnitude. Experimentally, Schönh et al. have prepared field-effect transistors using two-component self-assembled monolayers of conjugated and insulating molecules. Their results show that the conductance through the molecules can be varied by more than three orders of magnitude by changing the applied gate bias. Especially, using C$_{60}$ molecules, Champagne et al. have successfully demonstrated a single-molecule electronics device. Based on such a device one can adjust the spacing between the electrodes mechanically and simultaneously shift the energy levels in the molecule using a gate electrode.

As we know, Si is a semiconductor material with fundamental importance and potential applications in nanoelectronics. In this context, the study of the transport properties of Si$_n$ clusters in two-terminal and three-terminal devices is very important and necessary. However, the emphasis of previous theoretical investigations of Si$_n$ clusters was on the electron transport properties in the two-terminal devices. Therefore it is fundamental and practical to probe the transport behavior of the model device in the three-terminal system experimentally and theoretically. Moreover, for the experimental investigations of the transport properties of clusters, it is expected that more stable clusters are more advantageous to experimental observations. Among all Si$_n$ clusters, Si$_4$ is found to be the smallest magic number cluster with enhanced stability in the mass spectrum. In the current work Si$_4$ is then taken as a model cluster to investigate the transport behaviors in the three-terminal devices and to elucidate the effect of gating on the transport of Si$_n$ cluster theoretically. Our theoretical investigation is based on such a three-terminal system, where a Si$_4$ cluster is symmetrically sandwiched between two atomic scale Al(100) metallic electrodes (viewed as the source and drain electrodes, respectively) and an additional gate terminal is placed near the Si$_4$ cluster. The theoretical calculations are based on the combination of density-functional theory (DFT) with nonequilibrium Green’s function (NEGF) technique. Our results clearly show that an additional gate electrode has a great influence on the transport properties of Si$_4$ cluster and that the equilibrium conductance oscillates with the gate voltage. Furthermore, even in a three-terminal device Si$_4$ cluster exhibits negative differential resistance (NDR) behavior. Especially, it also displays negative transconductance when the drain voltage is fixed at a small value.

The organization of the paper is as follows: The computation method and the device model are briefly described in...
Sec. II; the results and discussions are presented in Sec. III; and a short summary is given in Sec. IV.

II. CALCULATION METHOD AND SIMULATION MODEL

The calculations have been performed by using the TranSIESTA-C package, which combines DFT (as implemented in the well-tested SIESTA method\textsuperscript{14}) with the NEGF technique. This approach allows us to calculate the transport properties of nanoscale devices that consist of an atomic scale system coupling with two semi-infinite electrodes as shown in Fig. 1 without inducing phenomenological parameters. Such a nanoscale device is divided into three parts for practical calculations: the left electrode, the right electrode, and the central scattering region. The scattering region actually includes a portion of the semi-infinite electrodes. To modulate the transport properties of such a device, an additional gate electrode with gate voltage $V_g$ can be positioned near the Si$_4$ cluster. In the current implementation of the TranSIESTA-C package, the electrostatic effect of the gate electrode is simulated by shifting the molecular projected self-consistent Hamiltonian, i.e., the renormalized molecular levels\textsuperscript{15} of the device. This corresponds to assuming that the gate electrode induces an external electrostatic potential localized to the cluster region. For the metallic electrodes, this will be a reasonable approximation.\textsuperscript{5,16,17} The simulation procedure of such a system is briefly as follows. First the electronic structure of the left and right electrode is calculated only once by TranSIESTA-C to get a self-consistent potential. This potential is shifted rigidly relative to each other by the external potential bias and provides natural real space boundary conditions for the Kohn-Sham effective potential of the central scattering region. Afterwards from the Green’s function of the central scattering region, we can obtain the density matrix and thereby the electron density. Once the electron density is known, the DFT Hamiltonian matrix, which is used to evaluate the Green’s function, can be computed using the above boundary conditions by means of standard methods. The renormalized molecular levels of the device will be shifted by the gate electrode. This procedure is iterated until self-consistency is achieved. Moreover, the current through the atomic scale system can be calculated from Landauer-Büttiker formula\textsuperscript{18}

$$I(V) = \frac{2e}{h} \int_{\mu_l}^{\mu_r} dE T(E, V_b),$$

where $\mu_l$ and $\mu_r$ are the electrochemical potentials of the left and right electrodes, respectively, i.e., for an applied bias $V_b$, $\mu_l(V_b) = \mu_l(0) + eV_b/2$ and $\mu_r(V_b) = \mu_r(0) - eV_b/2$. The energy region between $-eV_b/2$ and $+eV_b/2$, which contributes to the current integral above, is referred to as the bias windows. $T(E, V_b)$ is the transmission coefficient at energy $E$ and bias voltage $V_b$. Based on the eigenchannel decomposition of the conductance, this total transmission $T(E)$ can be decomposed into nonmixing eigenchannels $T_n(E)$ (Ref. 19) as

$$T(E) = \sum_n T_n(E).$$

For the system at equilibrium, the conductance $G$ is evaluated by the transmission coefficients $T(E)$ at the Fermi energy $E_f$ of the system

$$G = \frac{2e^2}{h} T(E_f).$$

Details of the method and relevant references can be found elsewhere.\textsuperscript{20–22} In our DFT calculation, the local-density approximation to the exchange-correlation potential, especially, the functional of Perdew and Zunger,\textsuperscript{23} is used. Only valence electrons are considered in the calculation, and the wave functions are expanded by localized numerical (pseudo)atom orbitals (PAOs).\textsuperscript{24} The atomic cores are described by norm-conserving pseudopotentials.\textsuperscript{25} The convergence criterion for the Hamiltonian, charge density, and band structure energy is $10^{-4}$ via the mixture of the Hamiltonian.

The structural model for our theoretical analysis is illustrated in Fig. 1. In such a Al-Si$_4$-Al system, the Si$_4$ cluster couples with two atomic scale Al(100) electrodes which extend to reservoirs at $\pm \infty$ where the current is collected. Four Al atomic layers have been chosen for the electrode cell in the $z$ direction, and a large enough vacuum layer is included in the electrode cell in the $x$ and $y$ direction so that the device has no interaction with its mirror images. Three atomic surface layers of the left electrode and four atomic surface layers of the right electrode are included in the central scattering region, indicated by the two vertical lines. These atomic layers in the central scattering region are large enough so that the perturbation effect from the scattering region is screened and they are denoted as surface-atomic layers. Motivated by the experimental ability to adjust the spacing between the electrodes and to shift the energy levels in the molecule using a gate electrode simultaneously,\textsuperscript{1} our theoretical investigation on the effect of the gate voltage also considers three cases with different source-drain separation $d$: 2.3, 3.0, and 3.6 Å. Moreover, based on a recently experimental indication\textsuperscript{1} that the largest applied gate voltage is $\pm 12.0$ eV, our calculations are performed for gate voltages in the range from $-12.0$ to $+12.0$ eV in steps of 0.2 eV. For the investigations on the nonequilibrium properties, two aspects are adopted. One is to probe the dependence of current on bias voltage for some fixed gate voltages. The other is to investigate the variation of current with the gate voltage for a small fixed bias voltage.
EFFECT OF GATING ON THE TRANSPORT...  

III. RESULTS AND DISCUSSIONS

A. Zero bias

Based on the method mentioned above, we first probe the effect of gate voltage on the equilibrium conductance for three different contact distances. The evolution of the equilibrium conductances with the gate voltage is presented in Fig. 2. As can be seen from this figure, for each fixed contact distance, the variation of the equilibrium conductance exhibits a striking oscillatory behavior as the gate voltage varies from $-12$ to $+12$ eV. Moreover, the extent of the conductance oscillating varies with the contact distance. At the same gate voltage, the equilibrium conductances are different for different contact distances. In particular, in the positive gate voltage region, the conductance decreases with the increase of the contact distance for each gate voltage. These performances demonstrate that the effect of gate voltage on transport properties of the atomic scale conductors is very closely related to the specific contact structure between the conductors and electrodes, for example, the separation. Meanwhile, from Fig. 2 we can find that opposite gate voltages with the same magnitude but with the different signs, i.e., $+V_g$ and $-V_g$, have different influences on the equilibrium conductance. In particular, the extent of conductance oscillating is more drastic in the negative gate voltage region than that in the positive gate voltage region. This is because the energy-level distribution of the Si$_4$ cluster is asymmetrical around the Fermi level. As the gate voltage shifts the energy levels of Si$_4$ cluster up or down with respect to the Fermi level, the shift direction of these energy levels is different for opposite $V_g$, resulting in the different alignment between the energy levels of Si$_4$ cluster and the Fermi level of the electrodes, and eventually causing different conductances. Within the gate-voltage range examined, it is shown in Fig. 2 that such a Si$_4$ cluster can convert from a high conductance state to a low conductance state due to the tuning of the gate voltage at a fixed contact distance $d$. Consequently, the conductance through such a magic cluster Si$_4$ is possibly modulated significantly by a gate potential, producing field-induced molecular switch behavior. In order to analyze how the equilibrium conductance varies with the gate voltages for three contact distances, we thus investigate the variation of the total density of state (DOS) at the Fermi level, presented in Fig. 3. Accordingly, DOS also oscillates with the gate voltage. Moreover, the influence of gate voltage on DOS at the Fermi level is also different in the positive and negative regions, respectively. Comparing the variation of the equilibrium conductance and DOS from Figs. 2 and 3, we observe that the positions of the peaks and valleys of DOS are the same as those of the equilibrium conductance. In other words, when DOS varies drastically the conductance also varies drastically. As a conclusion, it is believed that the shift of the energy levels of Si$_4$ cluster, as induced by $V_g$, changes DOS at the Fermi level, and eventually influences the transmission at Fermi level. Experimentally, the influence of DOS at the Fermi level on the transport properties of the mechanically deformed C$_{60}$ molecule has been demonstrated by Joachim et al.\textsuperscript{5,26} More interestingly, from Figs. 2(a)–2(c) and the mirrored Figs. 3(a)–3(c) one can find that the equilibrium conductance becomes increasingly symmetric with respect to the point zero of the gate voltage as the contact distance increases. Especially, in the conductance curve of 3.6 Å shown in Fig. 2(c), one can observe the discrete conductance peaks, which are more relatively separate and more symmetric than those in the other two cases. This can be understood as follows. When the cluster-electrode distance is small, the strong coupling between the cluster and electrodes has a very strong and complicated effect on the broadening and shift of the energy levels of the central Si$_4$ cluster. Therefore, the cooperation of the strong coupling and the gate voltage make the equilibrium conductance curve highly asymmetric and irregular with the variation of the gate voltage.

FIG. 2. The equilibrium conductance as a function of the gate voltage for different contact distances: (a) for $d=2.3$ Å; (b) for $d=3.0$ Å; and (c) for $d=3.6$ Å.

FIG. 3. The density of state (DOS) at Fermi level as a function of the gating voltage for different contact distances: (a) for $d=2.3$ Å; (b) for $d=3.0$ Å; and (c) for $d=3.6$ Å.
DAI et al.

FIG. 4. The transferred charge of the Si$_4$ cluster in the threeterminal system as a function of the gate voltage for the case $d=3.0$ Å, and a positive value means that electrons are transferred from the electrode to the cluster.

With increasing the contact distance up to 3.6 Å, the coupling between the cluster and electrodes becomes weak, and thus the broadening of the energy levels of the central Si$_4$ cluster caused by the coupling also becomes weak. This is manifested by the transmission spectra exhibiting the discrete transmission peaks in the case without the gate voltage, as illustrated in Fig. 3(d) of our previous work. With the application of gate voltages, these energy levels are shifted, correspondingly these transmission peaks are also shifted. Particularly, whenever these energy levels cross the Fermi level of the electrode, the equilibrium conductance takes a local maximum. Therefore, since the transmission spectra exhibits the discrete peaks in the case without the gate voltage, with the variation of the gate voltage the equilibrium conductance also displays the discrete peaks with more relative separation and thus seems more symmetric than those in the other two cases.

As far as we know, charge transfer is very closely related to the quantum transport properties of atomic scale conductors. In some systems, such as the C$_{60}$ molecular junctions, charge transfer may play a crucial role in the transport behavior. In such a system, charge transfer favors the aligning of the lowest unoccupied molecular orbital of the C$_{60}$ of the electrodes and then induces a substantial conductance. Once the charge transfer is inhibited by the gate voltage, a conductance gap is induced near the charge transfer is inhibited by the gate voltage, a conductance. In some systems, such as the C$_{60}$ molecular junctions, to the quantum transport properties of atomic scale conductors. Particular, whenever these energy levels cross the Fermi level of the electrode, the equilibrium conductance takes a local maximum. Therefore, since the transmission spectra exhibits the discrete peaks in the case without the gate voltage, with the variation of the gate voltage the equilibrium conductance also displays the discrete peaks with more relative separation and thus seems more symmetric than those in the other two cases.

FIG. 5. The transferred charge of the Si$_4$ cluster in the three-terminal system as a function of the gate voltage for the case $d=3.0$ Å.

In order to gain more insight into this oscillatory behavior of the equilibrium conductance with the gate voltages in the different contact distances, we carry out the eigenchannels decomposition of the total equilibrium conductance for the case $d=3.0$ Å, as presented in Fig. 5. First, one can clearly observe that the gate voltage does not change the number of the eigenchannels and the system holds three eigenchannels for the gate voltages from $-12$ to $+12$ eV. Especially, in the positive gate voltage region each eigenchannel significantly contributes to the total equilibrium conductance for each gate voltage. In the positive $V_g$ region, with the increase of the gate voltage, the transmission through eigenchannel $T_2$ almost remains unvaried. Thereby, the variation of the total equilibrium conductance is determined by the change in the transmission through the other two eigenchannels $T_1$ and $T_3$. Before $V_g$ increases up to 2.2 eV, the transmissions through $T_1$ and $T_3$ increase simultaneously with $V_g$ but with different varying rates. When $V_g$ is 2.2 eV the transmission through channel $T_1$ reaches saturation, and then the total conductance reaches a local maximum. With the further increase of gate voltage to 4.6 eV, the transmission through $T_1$ decreases with $V_g$ increasing. Although the transmission through $T_3$ increases with $V_g$, the cooperation of these two eigenchannels results in the appearance of a local minimum of the total conductance at 4.6 eV. As the gate voltage increases further, the transmission through $T_1$ first remains unvaried and then increases rapidly, however, the transmission through $T_3$ always increases steadily. When $V_g$ takes the value of 11.6 eV, both $T_1$ and $T_3$ saturate to unity, consequently, the total conductance again reaches a maximum. In the negative gate voltage region, by contrast, the influence of gating on the transmission through three eigenchannels is greater than that of the positive gate, accordingly, the oscillating extent of the total conductance in the negative $V_g$ region is also greater than that in the positive region. The whole negative gate
EFFECT OF GATING ON THE TRANSPORT...

FIG. 6. The current-voltage characteristics (I-V curves) of the Si₄ cluster in the three-terminal system under different gate voltages for \(d=3.0 \text{ Å}\). (a) For the positive gate voltages; and (b) for the negative gate voltages.

FIG. 7. The current-gate characteristics and corresponding transconductance of the Si₄ cluster in the three-terminal system for the case \(d=3.0 \text{ Å}\). The source-drain bias is fixed at 0.4 eV.

Voltage region can be divided into four regions. The first region is from 0 to \(−5.0 \text{ eV}\), in which the eigenchannel \(T₂\) is mainly responsible for the variation of the total equilibrium conductance as the gate voltage changes. Thus, at \(−2.0 \text{ eV}\), the appearance of the local maximum of the equilibrium conductance results from the saturation of the eigenchannel \(T₂\). Especially, when \(V_g\) is \(−5.0 \text{ eV}\), the transmissions through these three eigenchannels have been weakened simultaneously, which directly leads to the minimum value of the conductance. The second one is from \(−7.8\) to \(−5.2 \text{ eV}\), in which the total conductance is almost dominated by \(T₁\). When \(T₁\) saturates to unity at \(−6.8 \text{ eV}\), the conductance also takes a maximum correspondingly. The third one is from \(−10.0\) to \(−8.0 \text{ eV}\) and the last one is from \(−10.2\) to \(−12 \text{ eV}\). In these two regions, the equilibrium conductance is mainly determined by the eigenchannels \(T₂\) and \(T₃\), respectively. With the saturation of these two eigenchannels at \(−9.0\) and \(−10.0 \text{ eV}\), the equilibrium conductance takes a local maximum correspondingly. In the whole \(V_g\) region, it clearly shows that the equilibrium conductance reaches a maximum when one or two eigenchannels saturate to unity.

B. Finite bias

In order to systematically discuss the effects of the gate voltage on the transport properties of Si₄ cluster we also take the case of \(3.0 \text{ Å}\) as an example and investigate the nonequilibrium properties of such a system under different gate voltages via two aspects mentioned above. First, the I-V characteristics under some typical gate voltages are probed. The obtained I-V curves of Si₄ cluster in such a system as a function of the gate voltage are shown in Fig. 6, where Fig. 6(a) is for some typical positive gate voltages, and Fig. 6(b) is for some typical negative gate voltages. These figures clearly show that the Si₄ cluster still exhibits nonlinear I-V characteristics as in the zero gate case despite the modulation of the nonzero gate voltages. As elucidated in our previous work, a Si₄ cluster, which is symmetrically sandwiched between two atomic scale Al(100) electrodes, displays metallic I-V characteristics at small voltages; and a NDR behavior, in which the current decreases with increasing bias voltage, has also been found at higher biases. As can be observed from Fig. 6(a), the positive gate has a small impact on the nonequilibrium properties of such a cluster. These I-V curves share the same trend under different positive gate voltages. Even with the modification of positive gate voltage, a Si₄ cluster still exhibits metallic I-V characteristics under small drain biases, with a linear region between 0 and +0.6 eV. Under higher drain voltages between 0.8 and 1.4 eV, such a cluster also displays NDR. However, the negative gate voltage has a much greater influence on the I-V characteristics as shown in Fig. 6(b) than the positive gate voltage. Interestingly, there exists a NDR behavior for such a cluster under most gate voltages. The existence of NDR can be understood from the changes of coupling between the electrodes and Si₄ cluster under various drain biases, which has been analyzed in our early work by using the "significant energy regions" (SERs) model in detail.

For a molecular device to be a possible alternative to the conventional metal-oxide-semiconductor field-effect transistors, it is well-known that the gate voltage must be able to amplify the current by orders of magnitude at a fixed small source-drain bias. Therefore with the source-drain bias fixed at 0.4 eV, we investigate the current-voltage characteristics of the Si₄ cluster under different gate voltages, as presented in Fig. 7. From this figure, it can be observed that the gate voltage brings obvious variation in the current. As the gate voltage goes from negative values to 0 eV, the current first goes up and after exceeding a small negative gate voltage region, then the current goes down, leaving a peak of the current in the curve. When the gate voltage is \(−4.8 \text{ eV}\), a current minimum of 1.802 \(µ\text{A}\) appears. With further increase in the gate voltage from \(−4.8 \text{ eV}\) to positive values, the current increases steadily. The current amplification (from the zero gate field to the gate field investigated) is more than one order of magnitude. These results indicate that the conductance through a small cluster can be modulated by the field effect, leading to transistor behavior in a small cluster or a...
Energies are relative to the Fermi level.

Single molecule. The differential change of the drain current with the gate voltage for a constant drain voltage, named transconductance, is an expression of the performance of a bipolar transistor or field-effect transistor (FET). In general, the larger the transconductance for a device, the greater the gain (amplification) it is capable of delivering, when all other factors are held constant. With the drain voltage fixed at 0.4 eV, the transconductance is calculated and presented in Fig. 8. As shown in this figure, the transconductance fluctuates with the gate voltage. Moreover, in addition to NDR, this Si$_4$ cluster three-terminal device exhibits both positive and negative transconductance behaviors. These behaviors might have useful applications in the low-power logic circuits. Thus this three-terminal device is not only a potential molecular-scale alternative to current complementary metal-oxide semiconductor technology but also can provide some new molecular-scale logic applications. Experimentally, such positive and negative transconductance behavior has been found in some systems, for example, the carbon nanotube field-effect transistor, etc.29–31

To get further insight into these positive and negative transconductance behaviors, we present the transmission function $T(E, V_g)$ in Fig. 8. When a positive gate voltage is applied, the energy levels of the Si$_4$ cluster are shifted up. With the gate voltage gradually varied from zero to positive, it can be clearly seen that the transmission peak positions shift up, and thus move toward the Fermi level, even cross the Fermi level and eventually contribute to the current. As a result, the current increases with the gate voltage in this region.

IV. CONCLUSION

Based on a recently developed ab initio nonequilibrium Green’s function (NEGF) formalism, we have probed the effect of gate voltage on the transport properties of Si$_4$ cluster coupled with two atomic scale Al(100) electrodes. This effect has been investigated for three different contact distances based on a recent experimental indication. Our results imply that the transport behaviors of Si$_4$ cluster are significantly influenced by the gate potential. The equilibrium conductances greatly oscillate with the gate voltage for each contact distance, producing a field-effect molecule switch. This oscillatory behavior is very closely related to the variation of the system density of state at the Fermi level. Moreover, we have also demonstrated that the charge transfer is not the key factor to determine such a conductance oscillatory behavior. Using the eigenchannel decomposition of the conductance, we elucidate that gating does not change the eigenchannel number, and that the appearance of the conductance maximum results from the saturation of one or two eigenchannels. For finite biases, the Si$_4$ cluster exhibits a NDR behavior even under the influence of gating. Especially, it also displays a negative transconductance behavior for a small fixed drain bias.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation of China under Grant No 10374091, Knowledge Innovation Program of Chinese Academy of Sciences, and Director Grants of Hefei Institutes of Physical Sciences. Part of the calculations were performed in Center for Computational Science, Hefei Institutes of Physical Sciences. The authors also thank Dr. Bin Wang for useful discussions.

8Corresponding author. Email address: zzeng@theory.issp.ac.cn
8 C. Roland, V. Meunier, B. Larade, and H. Guo, Phys. Rev. B 66,
035332 (2002).