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First-principles study on the differences between the equilibrium conductance of carbon and silicon atomic wires

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Abstract

We perform first-principles calculations of the equilibrium conductance of carbon and silicon atomic wires coupled to two Al(100) nanoscale electrodes using the nonequilibrium Green formalism combined with the density functional theory. The conductance of atomic wires with quite a large range of number of atoms from $N = 3$ –20 is considered. Our calculations show that, for the carbon atomic wire, the equilibrium conductance as a function of the number of atoms (G – N relation) exhibits evident oscillatory behavior when the wire is not very long, and there is a big difference in conductance between the even-numbered wire and the odd-numbered wire. This difference becomes smaller and smaller with increasing wire length, until finally the conductance saturates to a constant value. The G – N relation for the Si atomic wires shows similar behavior when the number of atoms $N < 9$, but great differences appear when $N \geq 9$. Compared with the cases with numbers of atoms $N = 5$ –9 where the conductance of even-numbered wires is larger than that of the odd-numbered wires, the opposite result is obtained with $N = 10$ –14. As a whole, the conductance for Si wires shows an even–odd oscillatory behavior in a period of ‘ M ’ shape. The above behavior is analyzed via the charge transfer and the projected density of states (PDOS) and reasonable explanations are presented.

1. Introduction

Electron transport through atomic nanocontacts has been an active research area for a decade, both experimentally and theoretically, because such contacts represent the ultimate size limit of functional nanodevices [1–4]. Atomic nanocontacts are structures with low atomic coordination number and, as a result, they can behave very differently from their bulk counterparts. In fact, many valuable and interesting results have been found from atomic wires, including metallic nanowires, semiconducting nanowires and insulating nanowires [5–8]. For example, an even–odd numbered conductance oscillatory behavior was found in metal

Na [9, 10], Au [11] and Pt [11] atomic wires, and also the I – V curves through the atomic wires were strongly nonlinear. Things are very different for the Al atomic wires [12]. The conductance oscillates with a period of four atoms for wires with a typical interatomic spacing of 2.39 Å, but with another period of six atoms for wires with the interatomic spacing of bulk fcc aluminum, 2.86 Å. In experiments, fabrication of atomic wires has progressed along several lines. With the advantages of scanning tunneling microscopes or atomic force microscopes, an atomic wire can be formed between a sharp tip and a substrate and its electrical properties can be measured [13]. The atomic wire formed in this way can be extremely small, involving only a few atoms or

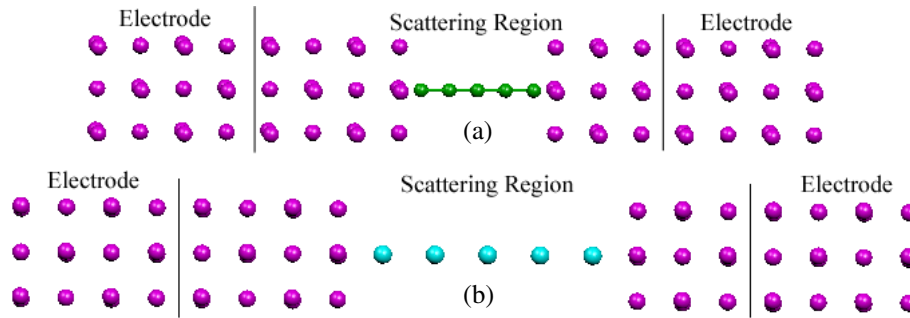


Figure 1. Model structure of an atomic wire sandwiched between two Al(100) nanoscale electrodes with finite cross-section: (a) for carbon; (b) for silicon.

(This figure is in colour only in the electronic version)

even just a single atom. In addition, substantial effort has been devoted to the fabrication of free-standing atomic wires using various methods [14]. For instance, several processes based on lithographic techniques have fabricated silicon or polycrystalline Si nanowires with sizes in the few-nanometer range [15]. A linear carbon atom wire, containing up to 20 atoms connected at the ends to metal atoms, has been synthesized [16], and so has an Si atomic wire [17].

Silicon nanowires (SiNWs) are promising building blocks for the bottom-up approach to nanoelectronics since the physical and chemical characteristics of SiNWs, including diameter, surface composition and electronic properties, can in principle be controlled during synthesis [17, 18]. Recently, several theoretical calculations have been done with the ultimately thin atomic wire of Si. By solving a three-dimensional quantum scattering problem and using a model of jellium electrodes, Mozos *et al* have calculated the conductance of Si atomic wires with up to eight atoms [6]. A conductance dip is found to develop near the onset of the second quantized plateau as the number of atoms increases. In a similar account, Okoano *et al* performed eigenchannel analyses of the electron transport in Si and Al atomic wires using jellium electrodes [1]. In 2005, Senger *et al* investigated conductance variations of monatomic Si wires in between Al electrodes as functions of wire length with a first-principles pseudopotential plane wave method [17]. An even-odd oscillation of conductance was found in Si atomic wires for the atom number range $N = 5-11$. Carbon atomic wires are interesting conductors and have attracted considerable attention recently [19, 20]. A linear atomic wire of carbon is even a better conductor than gold wire. In particular, due to charge transfer doping to the carbon atoms from the electrodes, the equilibrium conductance of short carbon wires varies with its length in a semiperiodic fashion. Such behavior is neither ohmic nor ballistic and therefore represents an interesting conduction behavior entirely due to the atomic nature of the carbon valence. In this paper we present a systematic study of the properties of equilibrium conductance in C and Si atomic wires with from 3 to 20 atoms in the wire and find some unexpected results. When the length of carbon atomic wire continues to increase, the conductance comes to be a constant. The conductance for Si wires shows even-odd oscillatory behavior in a period of ‘ M ’ shape.

2. Simulation model and calculation method

The simulation models for our calculations are illustrated in figure 1: a silicon atomic wire or a carbon atomic wire is sandwiched between two Al(100) nanoscale electrodes with semi-infinite cross-section. We have chosen a supercell with a large enough vacuum layer in the x and y directions so that the device has no interaction with its mirror images. In the calculations, the whole system is divided into three parts: the scattering region and the left and right electrodes. The atomic wire together with four surface atomic layers in the left electrode and three surface atomic layers in the right electrode is chosen as the central scattering region, as indicated by the two vertical lines. The electrode is extracted from a perfect Al crystal along the (100) direction, and the number of atoms in each atomic layer is arranged as 5, 4, 5, 4, ... Four Al atomic layers (5, 4, 5, 4) are selected for the electrode cell. The terminal atoms of the wires are positioned symmetrically above the Al(100) hollow sites. The contact distance between the atomic wire and the electrodes is fixed at $d = 1.0 \text{ \AA}$ for carbon wire and $d = 2.0 \text{ \AA}$ for silicon wire. The distance between carbon atoms is chosen as 1.323 \AA , and 2.348 \AA is chosen as the distance between silicon-silicon atoms. More details will be given later.

The calculations for transport properties were performed using a recently developed first-principles package, the TranSIESTA-C method, which is based on the nonequilibrium Green’s function (NEGF) technique. TranSIESTA-C, as is implemented in the well tested SIESTA method, is capable of fully self-consistently modeling the electrical properties of nanoscale devices that consist of an atomic scale system coupling with two semi-infinite electrodes as shown in figure 1. The potential in the semi-infinite electrodes provides natural real space boundary conditions for the Kohn–Sham potential of the scattering region, so the electronic structure of the two electrodes must be computed before the self-consistency procedure of the scattering region starts, but it will be calculated for only once. The coupling of the scattering region with the electrodes is taken into account by self-energies. Details of the method and relevant references can be obtained elsewhere [21, 22]. In our calculation, the convergence criterion for the Hamiltonian, charge density

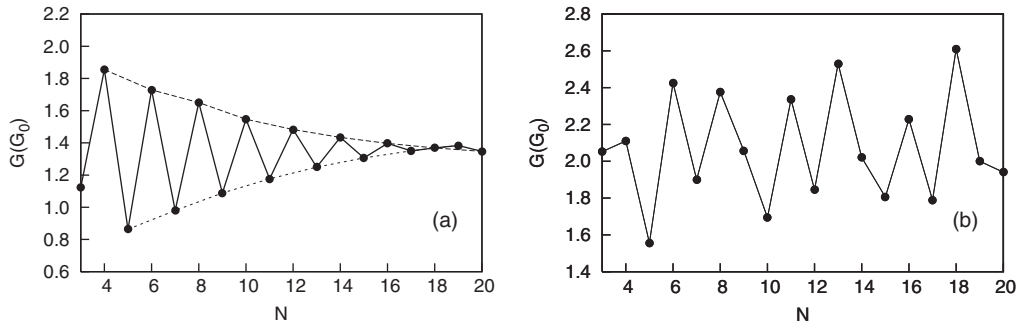


Figure 2. The conductance as a function of the number of atoms N : (a) for carbon wires; (b) for silicon wires.

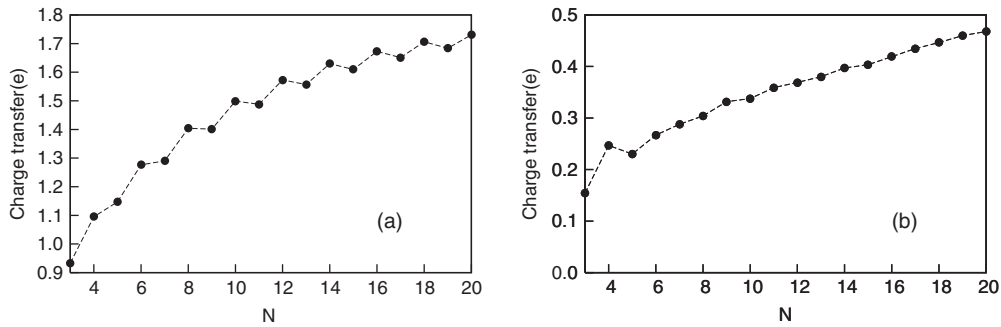


Figure 3. The charge transfer as a function of number of atoms N from the electrodes to the atomic wires: (a) for carbon wires; (b) for silicon wires.

and band structure energy is 10^{-4} and the atomic cores are described by norm-conserving pseudopotentials.

3. Results and discussion

To get the distance of two adjacent atoms in the atomic wires, we first calculate the bond length for an infinite wire by changing the lattice constants. For the structure with the lowest energy for the C wire it is 1.323 Å, while for Si wire it is 2.348 Å. Both values agree very well with the literature values [19, 23]. For all the wires with a finite length, an equal distance is chosen between each pair of nearest atoms, as done in the literature, and it is taken as the above values.

Figure 2 shows the equilibrium conductance as a function of atomic number N for carbon and silicon wires. From the figure, we can see that the conductance oscillates with the number of atoms N for both C and Si wires. For the carbon wire, if we focus on those wires with an odd number of atoms, we find that the conductance is increasing monotonically with N , while it is decreasing with N for even-numbered wires. Therefore, the conductance difference between the even-numbered wire and the odd-numbered one becomes smaller and smaller, and at last the conductance saturates to a constant. Things are greatly different for the silicon wires. Firstly, the conductance does not come to a constant when the number of atoms in the wire increases from 3 to 20; secondly, the conductance for the even-numbered wire is not always bigger than the odd-numbered wire, but shows an even-odd oscillatory behavior with a period of ‘M’ shape. Based on

the above facts, we want to ask the following questions: why does the conductance difference between the even-numbered and odd-numbered carbon wires become smaller and smaller with increasing N and finally saturate to a constant, while it is always oscillating with a random feature in Si wires? Why is the difference between the C and Si wires so big since they are from the same group in the periodic table?

It is well known that half-filled orbitals contribute to electrical conduction while full orbitals do not. So we can say that the closer the orbital is to being half-filled, the better the orbital conducts, while the closer the orbital is to being fully filled, the worse it conducts. According to Lang and Avouris [19], a free N -atom carbon wire has $(N - 1)/2$ fully occupied π orbitals when N is odd, and $(N/2) - 1$ π full occupied orbitals and one half-filled orbital when N is even. In our calculations, the charges transferred from the electrodes to the carbon wire are studied for all the cases, as shown in figure 3. The number of transferred charges increases with increase in the number of atoms for both odd- and even-numbered carbon wires. When we look at it as a whole, the charge transfer increases in an even-odd oscillating way. It is known that odd-numbered free carbon wires have a fully occupied highest occupied molecular orbital (HOMO) level. Under the interaction of the electrodes, the lowest unoccupied molecular orbital (LUMO) will be partially filled due to the charge transfer from the electrodes. Because the number of the charge which the wires get from the electrodes increases quickly and becomes closer and closer to two electrons (in other words, the LUMO is closer and closer to being half-filled) the conductance of an odd-numbered wire increases with

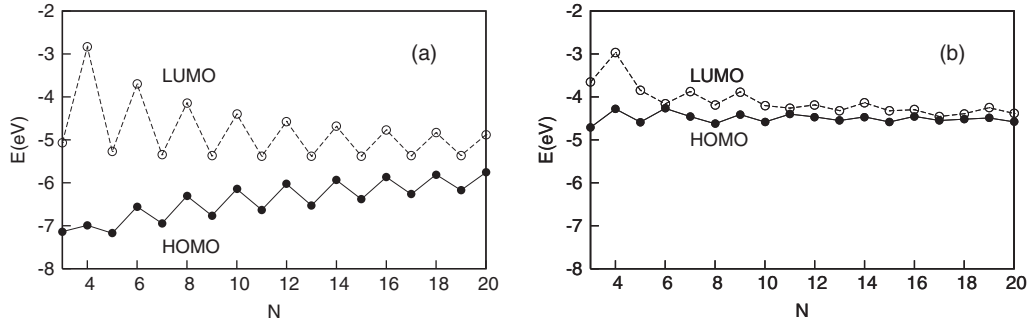


Figure 4. The evolution of HOMO and LUMO as a function of the atom number: (a) for C wires; (b) for Si wires.

the increase in the number of atoms. The even-numbered free wires, however, have a half-filled HOMO. When they are placed between the Al (100) electrodes, with the increase in the number of atoms the number of electrons transferred from the electrodes to the wires increases and becomes nearer and nearer to two, so this HOMO becomes fuller and fuller. That is the reason why the conductance of the even-numbered wires decreases with increasing length of the wire. From the above, we understand why the conductance difference between the even-numbered and odd-numbered carbon wires becomes smaller and smaller.

The silicon atom, though it has the same number of valence electrons as the carbon atom in the outermost layer, has three layers outside the atomic nucleus, which is one layer more than that of the carbon atom. This makes it harder to get electrons, which can also be seen from figure 3(b) where the charge transfer from the electrodes to the silicon wire is much smaller than that for the carbon wire. The maximum number of the transferred charge is just about $0.45e$, which has a rather smaller influence on the conductance. In particular, we do not see a clear even-odd oscillating behavior in the change of the charge transfer as in the carbon atomic wires.

It is interesting to notice that both the conductance and the charge transfer have the same oscillating period, namely 2, in the carbon wires, while the oscillating feature in the silicon wires is different. At least, for the carbon wires, we can see that the conductance is closely related to the charge transfer. Then what determines the charge transfer in these systems? A natural factor is the alignment evolution of the LUMOs or the half-filled HOMOs of the atomic wires with the Fermi level of the electrode. Therefore, we plot the evolution of the HOMO and LUMO of the atomic wires as a function of atom number in figure 4. We find that, in the carbon wires, the energy of the LUMO and HOMO also oscillate in the same way as the charge transfer and the conductance, namely, with a period of 2. This is easy to understand, since the even-odd oscillation of the LUMO and HOMO will affect the charge transfer and further affect the conductance in the carbon wire. In comparison, the energy of the LUMO and HOMO in the silicon wires oscillates in a completely different way and the oscillation magnitude is much smaller. Correspondingly, we cannot clearly see the oscillation of the charge transfer in them.

For carbon wires, charge transfer is enough to account for the oscillating behavior, while for silicon wires we cannot

get enough information from the charge transfer alone to understand its oscillating conductance. To further understand the reason for the even-odd oscillatory behavior with a period of ‘ M ’ for Si wire, we calculate $n(E)$ (PDOS as a function of the incident electron energy E) for each Al(100)–Si wire–Al(100) structure. Here we just choose the $n(E)$ for wires with number of atoms ranging from 5 to 12, as shown in figure 5, which will be enough to explain the conductance behavior. The density of states of the combined system projected onto the basis orbitals of the silicon wires is calculated by $P(E) = \langle \varphi^m(E) | \psi(E) \rangle = \sum_i^{\text{mol}} c_i(E) \phi_i(\vec{r}) | \sum_j^{\text{all}} c_j(E) \phi_j(\vec{r})$, where $\psi(E)$ is the eigenstate of the whole system and $\varphi^m(E)$ is the contribution of the basis orbitals of the atomic wire to $\psi(E)$, $\{\phi\}$ is the nonorthogonal basis set of the system, and c_i and c_j are expanding coefficients. The sum over i runs over the basis orbitals of the atomic wire, and the sum over j runs over all the basis orbitals of the whole system. The PDOS will give us information on how much the basis orbitals in the atomic wire contribute to the eigenstate of the whole open system and how strongly the molecule couples with the electrodes at a certain energy E [24]. We can see in figure 5 that when the number of atoms in the wire is 5, 7, 9 or 10, the PDOS at the Fermi energy ($E = 0$) is at the valley or near the valley in the curve. Then we can conclude that the Si wire with $N = 5, 7, 9$ or 10 atoms has rather weak coupling with the electrodes at the Fermi energy. A weak coupling makes incident electrons at a certain energy hardly transmit across the wire and this leads to a low transmission coefficient at this energy. This can be verified by the transmission curve $T(E)$ for the cases when $N = 5, 7, 9$ or 10 where the transmission coefficient is at the valley or near the valley at the Fermi energy (see figure 6). While for Si wire with the $N = 6, 8$ or 11 atoms it is completely different. The coupling between the wire and the electrodes is comparatively strong at the Fermi energy which can be seen from figure 5 for $N = 6, 8$ or 11 where the PDOS reaches its peak value at the Fermi energy. Then strong coupling gives rise to the high transmission for the wires with $N = 6, 8$ or 11 atoms, which can be also proved in figure 6. Then an even-odd oscillatory behavior occurs with a period of ‘ M ’ for Si wire. To sum up the above arguments, the reason for the even-odd oscillatory behavior with a period of ‘ M ’ for Si wire is determined by the coupling between the wire and the electrodes.

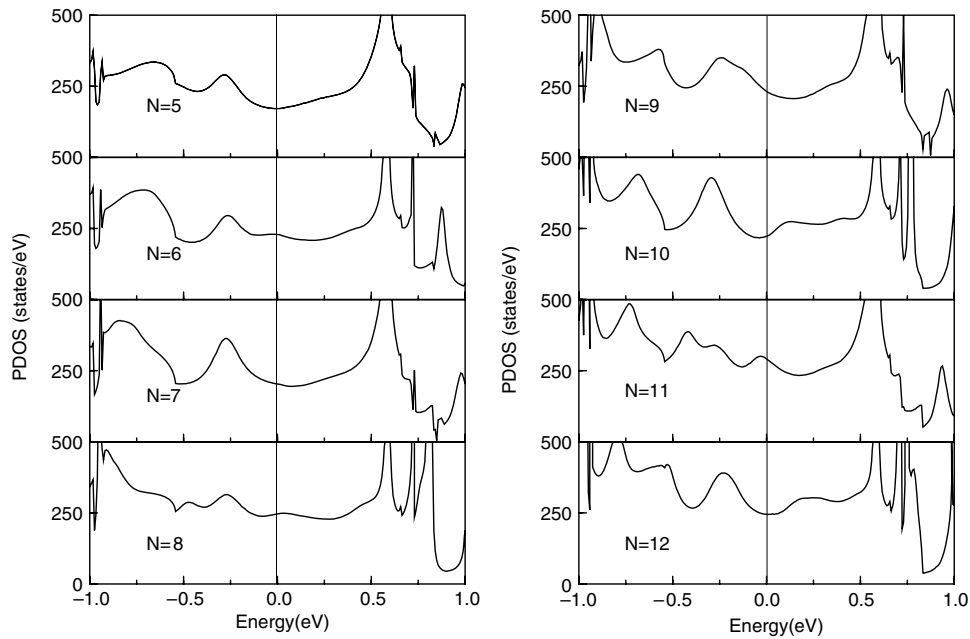


Figure 5. The PDOS as a function of the incident electron energy E for the Al(100)–Si wire–Al(100) system with $N = 5$ –12 silicon atoms, respectively.

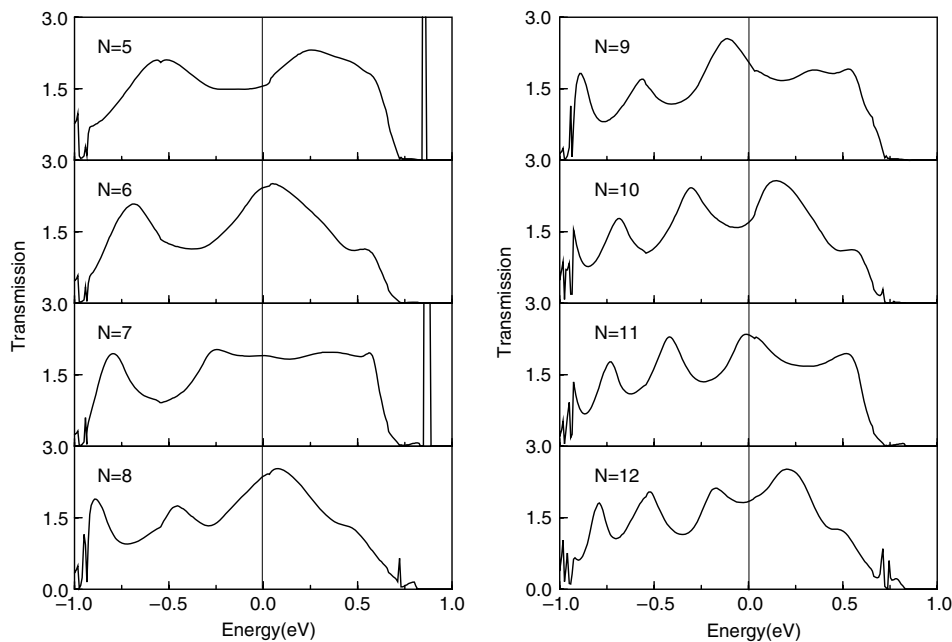


Figure 6. The transmission function for the Al(100)–Si wire–Al(100) system with $N = 5$ –12 silicon atoms, respectively.

4. Conclusion

First-principles calculations based on density functional theory are presented to study the equilibrium conductance of carbon and silicon atomic wires coupled to two Al(100) nanoscale electrodes. Some interesting phenomena are found. For the carbon atomic wire, the equilibrium conductance as a function of the number of atoms exhibits evident oscillatory behavior when the wire is not very long. The conductance of the even-numbered wires is monotonically decreasing and

is monotonically increasing in the odd-numbered wires. So there is an obvious conductance difference between the even-numbered wire and the odd-numbered wire, but this difference becomes smaller and smaller with increasing wire length, until finally the conductance becomes constant. Interestingly, the conductance, charge transfer and the LUMO/HOMO all oscillate with the same strict even–odd period in the carbon wires. The G – N relation for the Si atomic wires shows similar behavior when the number of atoms $N < 9$, but great differences appear when N exceeds 9. The conductance

of the even-numbered wires is larger than that of the odd-numbered wires with $N = 5-9$, while an opposite result is obtained for $N = 10-14$. As a whole, the conductance for Si wires shows even-odd oscillatory behavior in a period of ' M '. This unusual behavior can be understood in terms of coupling between the silicon wires and the electrodes and the coupling may be measured to some extent by the PDOS. In fact the coupling is associated with many elements, such as the structure and the kind of the electrode, the central conductor, and the contacts between them and so on, all of which will make some contribution to the PDOS.

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