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Bias-dependent oscillatory electron transport of monatomic sulfur chains

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The bias-dependent oscillatory electron transport of monatomic sulfur chains sandwiched between gold electrodes is investigated with density functional theory and non-equilibrium Green's function method. At zero bias, in contrast to the typical odd-even oscillations observed in most metallic chains, we find that the conductance oscillates with a period of four atoms. However, as the bias voltage is increased the current displays a two-atom periodicity. This emerges gradually, first for the longer chains and then, at voltages larger than 0.7 V, for lengths. The oscillatory behaviors are analyzed by the density of states and the energy-dependent and bias-dependent transmission coefficients. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3693380>]

In recent years, Au, Cu, and other metallic nanowires and nanotubes suspended in two thimble tips in ultra-high vacuum have been the prepared and characterized experimentally, with typical wire diameters smaller than 1 nm and lengths larger than 6 nm.^{1,2} A single-atom chain is formed when the size of an ultra-fine nanowire further reduces. These one-dimensional objects represent a peculiar morphology, which shares with clusters the atomic scale dimensions. Ohnishi *et al.*³ early in 1998 were able to make suspended Au monatomic chains by scanning tunneling microscopy (STM) experiments and measured their conductance to be $G_0 = 2e^2/h$ (G_0 is the quantum conductance, e the electron charge, and h the Planck constant). Similarly, Yanson *et al.* produced Au monatomic chains by mechanically controlled break junctions (MCBJ) (Ref. 4) and obtained similar conductance values. A major breakthrough occurred in 2008 when the structural information about the electrodes and the crystalline orientation of the nanowires were measured with atomic precision by STM.⁵ The study of the various properties of monatomic chains such as the anomalous dependence of the resistance on the chain length,⁶ the presence even-odd conductance oscillations⁷ and of possible negative differential conductances⁸ is particularly useful in order to understand the metallic state of nanoscale objects.

These early experiments inspired a surge of theoretical calculations. In particular, the conductances of Al,^{9,10} Nb,¹⁰ Pt,¹¹ Pd,¹¹ Na,¹² Ni,¹³ Cu,¹⁴ Au,^{15–17} Xe,¹⁸ Si,¹⁹ and C (Ref. 20) monatomic chains have all been computed by using tight-binding approaches,^{10,13} the recursive transfer-matrix (RTM) scheme^{12,14,15} and density-functional theory combined with the non-equilibrium Green-function method (DFT+NEGF).^{16–20} Many of these works revealed an interesting oscillatory behavior of the zero-bias conductance as the chain length is increased. Smit *et al.*²¹ found that the conductance of monovalent Au, Pt, and Ir atom chains oscillate in an even-odd fashion with the number of atoms in the chain and they argued that this is a universal feature of monatomic wires. Lee *et al.*²² studied chains made of monovalent alkali-

metals (AM) and noble-metals (NM) and found that the conductance of the NM chains oscillates as a function of the chain length so that its maxima (minima) occurs at an even (odd) number of atoms in the chain. This contrasts to what happens for AM-based monatomic wires, where the oscillations have the opposite phase. Lang and Avouris²⁰ showed that the conductance of odd-numbered carbon-atom chains is higher than that of even-numbered chains and that a stronger electronic coupling between the chains and the electrodes does not necessarily implying a higher conductance. Finally, Thygesen and Jacobsen²³ found that the conductance of Al wires has an oscillatory character with a period of four atoms, thus disproving the general conclusion of Smit *et al.* about the two-atom period of oscillations.²¹

Recently, we have investigated the transport properties of S_9 sulfur clusters, which show strong bonding to Au and still good conduction,²⁴ and explored four different Au(100)- S_2 -Au(100) nanoscale junctions, which show that the junction connected to pyramical-shaped Au electrodes at the top site has good conduction.²⁵ In this letter, we focus on S_n monatomic chains connected to pyramical-shaped Au electrodes at the top site, and investigate the electron transport as a function of size (n). In particular, we study both the zero-bias conductance and the finite-bias current for chains comprising between 1 and 12 sulphur atoms. Our calculations showed that the zero-bias conductance varies in an oscillatory manner with the number of atoms in the chain. However, the period of the oscillation is four-atom long similar to that of Al wires.²³ Intriguingly, the oscillation period changes as the bias is increased and already at relatively moderate voltages odd-even oscillations are recovered.

The transport properties are calculated with *ab initio* quantum transport code SMEAGOL,^{26,27} which combines the NEGF (Ref. 28) formalism with DFT.²⁹ SMEAGOL uses the single-particle Kohn-Sham Hamiltonian provided by DFT calculations performed with SIESTA,³⁰ and it evaluates the zero-bias electron transmission coefficients and the I - V curves of a two-terminal device. In particular, SMEAGOL is capable of fully self-consistent calculations of the electrical properties of devices formed by an atomic-scale object attached to two semi-infinite current/voltage electrodes, i.e., it calculates the

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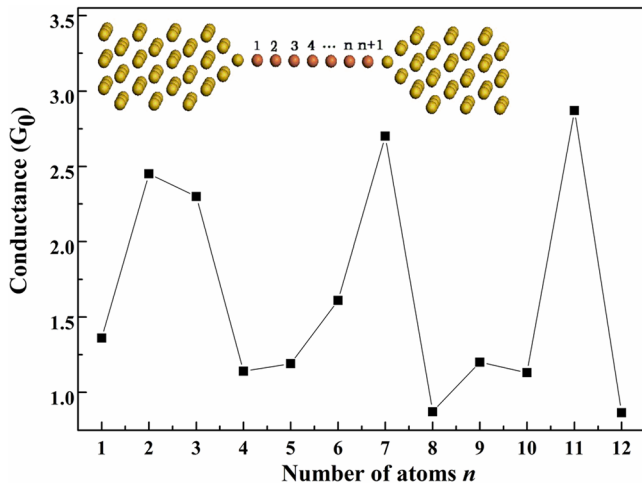


FIG. 1. (Color online) Calculated zero-bias conductance as a function of the number of sulfur atoms in the S_n chain ($n = 1$ to 12). The inset shows the geometry of the device investigated.

scattering potential at finite bias. Our calculations use the Perdew-Zunger form³¹ of the local density approximation (LDA) to the exchange-correlation functional. Scalar-relativistic Troullier-Martins pseudopotentials³² generated from $5d^{10}6s^1$ for gold and $3s^23p^4$ for sulfur are employed. To make the calculations more tractable and reduce the computational overheads, a single ζ is used as the basis set for Au, and a double ζ basis is adopted for the orbitals of the S atoms. The charge densities and the DFT potential are computed on a real-space grid with cut-off energy of 200 Ry, which is also used in the self-consistent transport calculations. An electrical temperature of 300 K is used throughout the calculation and periodic boundary conditions are applied in the basal plane (orthogonal to the transport direction) with four irreducible k -points in the two-dimensional Brillouin zone. A k -grid sampling of $2 \times 2 \times 100$ for Au electrodes is employed. Finally, we consider 128 real and 50 complex energy points when integrating the Green function.

A snapshot of our point contact geometry is presented in Fig. 1 where an n -site-long chain is sandwiched between two Au electrodes oriented along the (100) direction and terminated with a pyramidal apex. Atomic relaxation is performed first by conjugated gradient, where we also relax the five Au atoms binding the S_n chain to the current/voltage leads (the pyramid atoms). A locally stable configuration is found by changing the distance between the end atoms of the chain and the apexes of the point contact. Our results showed that in all the stable structures the chains remain linear and symmetric about its center. The Au-S bond length agrees well with the experimental value ($2.3 \sim 2.4 \text{ \AA}$).³³ The average S-S distance \bar{d} is 2.20 \AA , which is much larger than the interatomic spacing in bulk S, 1.889 \AA . Such an extended bond length for monatomic chains with respect to bulk is the result of the different coordination and it has been already observed for other metals like Au.³ If we examine the S-S bond distribution, we observe that this depends on the parity of the chain. Odd chains present a uniform bond length of $2.20 \pm 0.03 \text{ \AA}$, however, even chains are characterized by bond length alternation, with short and long bonds of $2.14 \pm 0.02 \text{ \AA}$ and $2.26 \pm 0.03 \text{ \AA}$, respectively. This means that Peierls distortion³⁴ is strongly active only in even chains.

Fig. 1 also shows the zero-bias conductance, G , as a function of the number of sulfur atoms n in the atomic chain (i.e., of the chain length). We observe that the conductance does not decrease with increasing chain length nor it does exhibit the even-odd oscillations. In contrast, it presents an oscillatory behaviour with a period of four S atoms. Well pronounced maxima appear at $n = 3 + 4m$ while the minima are at $n = 4m$, where m is an integer. This oscillatory conductance can be rationalized by the resonant transport model proposed first by Thygesen and Jacobsen.²³ The main idea is that the electron transport occurs via resonances at the S_n atomic chain energy levels. In general, by assuming that the coupling between the S_n chains and the electrodes is energy

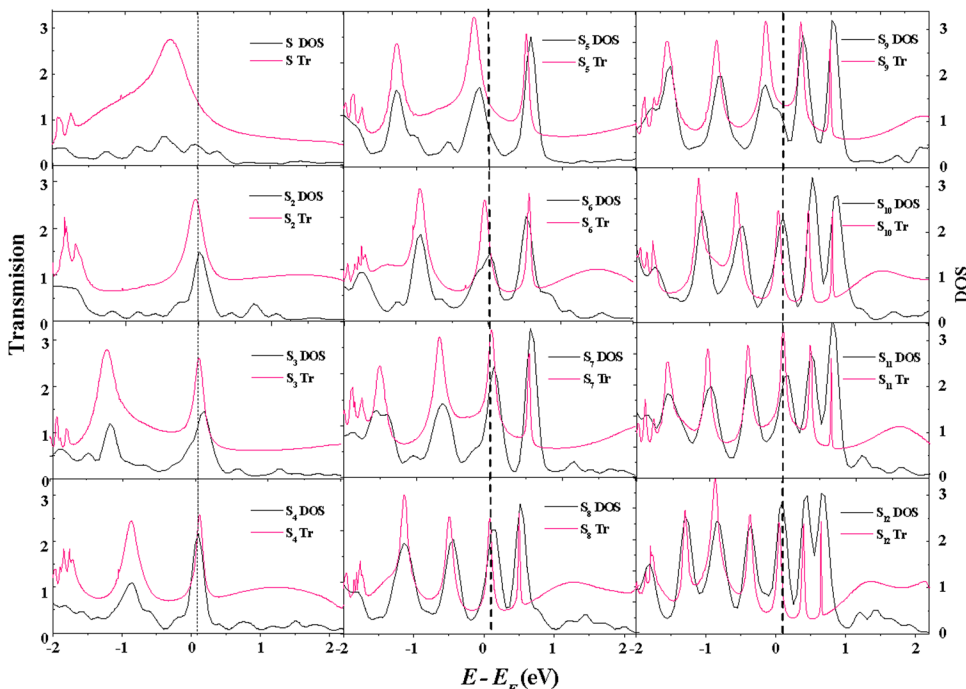


FIG. 2. (Color online) Transmission coefficient at zero-bias and DOS as a function of energy for various S_n chains ($n = 1$ to 12) attached to the Au(100) electrodes.

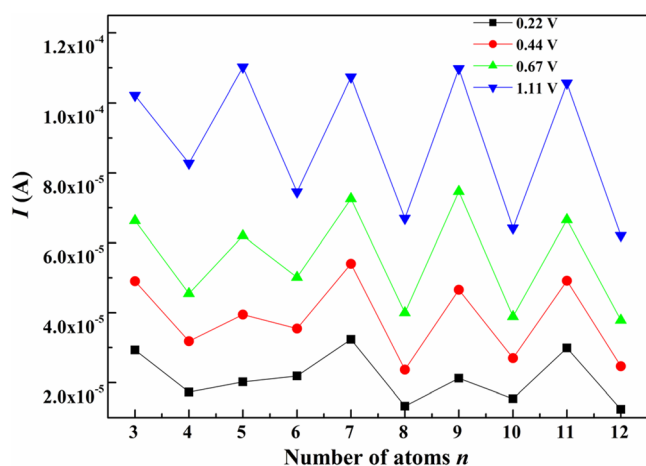


FIG. 3. (Color online) Current, I , calculated at different bias voltages as a function of the number of sulfur atoms in the S_n chains ($n = 3$ to 12).

independent, one expects that the width of the resonances varies as $1/n$ with the chain length. The transport is then solely determined by the position of such broadened energy levels with respect to the electrode Fermi energy E_F .

In Fig. 2, we present the density of states (DOS) and the energy-dependent zero-bias transmission coefficient for all chains with $n = 1$ to 12. In particular, we include the DOS states belonging to the atomic chain and to the two outermost atoms in the Au tips. In general, the DOS presents a number of discrete peaks, corresponding to the various molecular orbitals of the chain. These correlate well with the energy dependent transmission function so that a peak in the DOS corresponds to a peak in the transmission. The zero-bias conductance is then determined by whether Au Fermi level is positioned in a peak or in a valley of the DOS. In the case of a single S atom, E_F is positioned in a relatively featureless region of the DOS and cuts through the tail of a transmission peak. As such the overall zero-bias conductance is rather small. Different is the situation for both S_2 and S_3 , for which the Fermi level is pinned at a peak in the DOS and the transmission is large. A further increase of the chain length adds

molecular orbitals and shifts the chain spectrum with respect to Au Fermi level. For both S_4 and S_5 the Fermi energy is now in between two peaks in the DOS and the transmission is again small, while for S_6 and S_7 , a peak pins the Fermi level and the transmission is again large. This pattern repeats to all the other lengths investigated and the oscillatory behavior of Fig. 1 is obtained.

We next investigate how the oscillation pattern changes upon the application of an external bias. This is summarized in Fig. 3, where we present the current as a function of chain length for four representative bias voltages, namely 0.22 V, 0.44 V, 0.67 V, and 1.11 V. The most notable feature emerging from the figure is a gradual change of the oscillation period from two to four atoms as the bias increases. Such a period change starts first for longer chains but then it gradually develops at all lengths. For instance already for a voltage of 0.67 V a period of two is observed for $n > 3$. An insight into such a behavior can be obtained by looking at the transmission coefficient as a function of bias presented in Fig. 4 for $n = 5-8$.

We remind here that the current is just the integral of $T(E;V)$ over the bias window around the Fermi level (this interval is marked in the figure with vertical lines), so that as the bias is increased a larger portion of the transmission spectrum determines the transport. From Fig. 4, one can immediately conclude that there is little modification in the transmission function of the various S chains as the bias gets larger, i.e., there are no significant changes in either the position of the transmission resonances or their broadening. This suggests that the S chains undergo little charge transfer and/or electrical polarization upon bias.³⁵ As such, it is solely the enlargement of the bias window to produce the change in the periodicity. For instance, in the interval $n = 5-8$ the two-atom period is obtained because of a significant increase of the current of the S_5 chain with respect to those of others S_n (note that the current gets larger for all chains as the bias is increased). This is simply due to the fact that the dominant transmission peak corresponding to the S_5 HOMO level progressively enters the bias window. At 1.11 V the HOMOs of

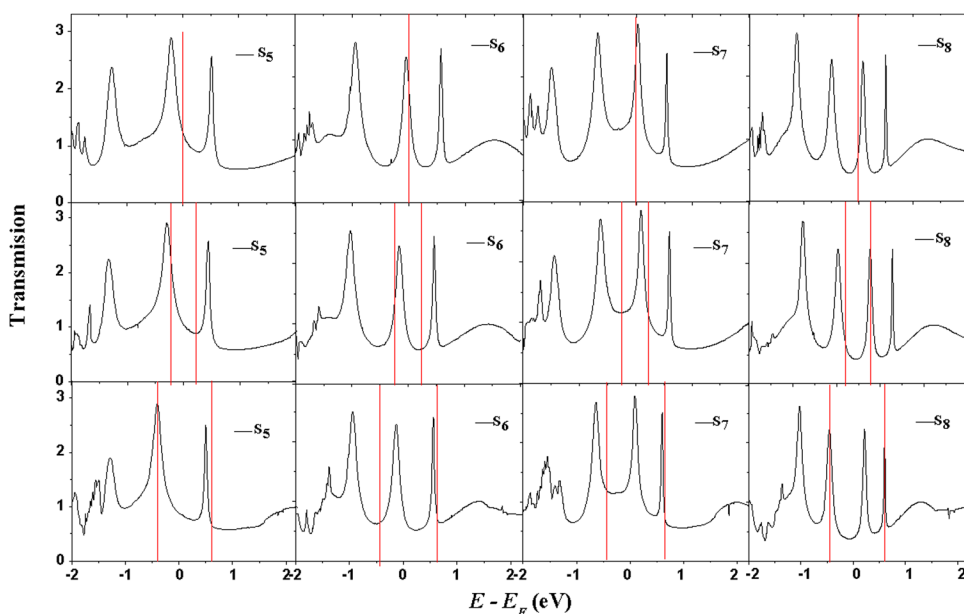


FIG. 4. (Color online) The transmission coefficient as a function of energy at different biases for number of sulfur atoms ($n = 5$ to 8) attached to the Au(100) electrodes. The column of top, middle, and bottom is at zero, 0.44 V, and 1.11 V, respectively. The vertical lines is respected the bias windows.

both S_5 and S_6 are entirely within the bias window, but that of S_5 gives a significantly larger contribution to the current, as the peak value of the transmission function is larger. Furthermore for S_5 the high-energy boundary of the bias window cuts right across a second transmission peak (the one corresponding to the LUMO), which provides additional contribution to the current. The same does not hold true for S_6 where the same boundary is placed just before the LUMO resonance.

In conclusion, we have presented a DFT-NEGF study of the electron transport across sulfur monatomic chains connected to Au(100) electrodes. We find that the chains remain straight and symmetric with respect to the electrodes, with a uniform lattice constant in the case of odd-numbered chains and with a significant Peierls distortion for the even-numbered ones. The zero-bias conductance displays an intriguing four-atom periodicity with the chain length, similar to that previously found for Al monatomic wires, however, the oscillation period reduces to only two atoms as finite bias is applied, with the change developing first for the longest chains and then, at biases in the 1 V range, for all the lengths investigated. The oscillatory behaviors are further analyzed by the device DOS and the energy-dependent and bias-dependent transmission coefficient of S chains containing Au electrodes.

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