Compositional ordering and quantum transport in Mo$_6$S$_9$–$x$I$_x$ nanowires: *Ab initio* calculations

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We use *ab initio* calculations to study the compositional ordering and quantum transport in Mo$_6$S$_9$–$x$I$_x$ nanowires. The skeleton of these nanowires consists of Mo octahedra, which are functionalized by S and I adsorbates and connected by flexible S$_3$ bridges. The optimum geometries and relative stabilities at different compositions are determined by using density functional theory. We find nanowires with $x=3$ to be particularly stable. Nanowires with other compositions are likely to phase separate into iodine-rich and iodine-depleted domains, some of which should have the Mo$_6$S$_9$I$_3$ stoichiometry. Our transport calculations, which are based on the nonequilibrium Green’s function formalism, indicate that the nanowires are metallic independent of composition and exhibit a quantum conductance of $G=3G_0$, with the three conductance channels involving the S$_3$ bridges.

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I. INTRODUCTION

Combining subnanometer diameter with structural stability and interesting electronic properties, transition metal chalcogenide nanowires have been discussed as a potentially viable alternative to carbon nanotubes for many applications. In particular, Mo$_6$S$_9$–$x$I$_x$ nanowires have been extensively studied both experimentally and theoretically. Nanomechanical studies indicate a stable compounds. X-ray Diffraction and extended x-ray absorption fine structure studies agree in the identification of Mo octahedra as stable building blocks of the nanowires. Sulfur terminators act as “alligator clips,” providing optimum contact to gold leads for molecular electronics applications.

In spite of the numerous studies, several questions about Mo$_6$S$_9$–$x$I$_x$ nanowires still await a definitive answer. There is a consensus that the skeleton of these systems consists of Mo octahedra, which are functionalized by S and I adsorbates and connected by bridges containing S or I atoms. Still, there is an open controversy about the atomic arrangement in nanowires with $x=4.5$ and $x=6$, which have been observed as stable compounds. X-ray Diffraction and extended x-ray absorption fine structure studies agree in the identification of Mo octahedra as stable building blocks of the nanowires but disagree about the precise positions of sulfur and iodine. In particular, both iodine and sulfur have been proposed as constituents of the bridges connecting the Mo octahedral building blocks. An additional uncertainty exists, which is whether the connecting bridges contain three or four atoms.

Obviously, the atomic structure plays a key role in determining the stability and conductance of the nanowires. In spite of the apparent interest in the topic, no conductance data are available that would illustrate the potential of Mo$_6$S$_9$–$x$I$_x$ nanowires sandwiched between gold leads for molecular electronics applications. Besides the available structural results for nanowires with $x=4.5$ and $x=6$ stoichiometries, which were assumed to be homogeneous, nothing is known about the structural properties of nanowires with other compositions, which may phase separate into iodine-rich and iodine-depleted domains. Lack of precise structural information also offers a plausible explanation for the apparent discrepancy between the measured and calculated Young’s modulus of Mo$_6$S$_9$–$x$I$_x$ nanowires with $x=4.5$ and $x=6$.

To address these open points, we combined *ab initio* density functional theory and quantum transport calculations based on the nonequilibrium Green’s function formalism to determine the stability, equilibrium structure, and electronic and transport properties of Mo$_6$S$_9$–$x$I$_x$ nanowires in the full composition range. We found the Mo$_6$S$_9$I$_3$ nanowire to be particularly stable and identify stoichiometries wherein separation into two phases, one of them being $x=3$, is energetically favorable. Sulfur-terminated wire segments are known to form optimum contacts to gold leads. We find that sulfur forms the most stable bridges connecting the functionalized Mo octahedra and determine the relative stability of bridges containing three or four sulfur atoms. Finally, we determine the conductance of Mo$_6$S$_9$–$x$I$_x$ nanowires with $x=3$ and $x=4.5$ sandwiched between two gold leads.

II. THEORY

To determine the optimum geometry, relative stability, and ground-state electronic structure of the nanowires, we used the density functional theory (DFT) as implemented in the SIESTA code. We used the Perdew–Zunger form of the exchange-correlation functional in the local density approximation to DFT. The behavior of valence electrons was described by norm-conserving Troullier–Martins pseudopotentials with partial core corrections in the Kleinman–Bylander factorized form. We used a double-zeta basis, including initially unoccupied Mo 5$p$ orbitals. We studied the possibility of spin polarization by using the local spin density approximation and found all the nanowires investigated here to be nonmagnetic.

To test the usefulness of these systems as ballistic conductors, we calculated the quantum conductance of Mo$_6$S$_9$–$x$I$_x$ nanowires sandwiched between two Au(111) surfaces as a...
function of the carrier injection energy $E$. Our calculations were performed by using the nonequilibrium Green's function approach, as implemented in the TRAN-SIESTAC code, and the localized basis set described above.

Our studies focus both on the infinite nanowires and their building blocks, which are depicted in Fig. 1. Infinite nanowires are represented by a periodic arrangement of unit cells with length $a$ containing 30 atoms in 2 formula units of the $\text{Mo}_6\text{S}_{12-}\text{I}_x$ compound. To describe isolated nanowires while using periodic boundary conditions, we arranged them on a tetragonal lattice with a large interwire separation of 30 Å. We sampled the rather short Brillouin zone of these one dimensional structures by six $k$ points. The charge density and potentials were determined on a real-space grid with a mesh cutoff energy of 150 Ry, which was sufficient to achieve a total energy convergence of better than 2 meV/atom during the self-consistency iterations.

III. RESULTS

A. Optimum functionalization of the building blocks in nanowires

To get a better understanding of the optimum arrangement of iodine and sulfur ligands on the $\text{Mo}_6$ octahedral building blocks in the nanowires, we optimized the structure of all the possible ligand arrangements in $\text{Mo}_6\text{S}_{12-}\text{I}_x$ systems. To avoid complications caused by stoichiometry-dependent unit cell sizes, we first considered finite nanowire segments. The wire segments were terminated on both sides by sulfur trimers as reference ligands, which act as bridge connectors in the infinite nanowire. Such chalcohalide clusters have been observed in cluster compounds, with a particular oxidation state stabilized by counterions. Even though we consider charge neutral wire segments, the electron count on the $\text{Mo}_6$ octahedra may differ from the infinite nanowire due to the presence of ligands on both sides, causing minor structural and energetic changes. Our results for the equilibrium structure of these finite building blocks with the 0 $\leq x \leq$ 6 composition are shown in Fig. 1. For the sake of a fair comparison, we oriented the $\text{Mo}_6$ clusters along the nanowire direction, which is indicated by the arrows, and visually grouped the different structural isomers with the same composition.

Our choice of using sulfur reference ligands is inspired by the results of the combined scanning transmission electron microscopy and x-ray photoelectron spectroscopy study of $\text{Mo}_6\text{S}_3\text{I}_x$ nanowires, suggesting that all bridges connecting $\text{Mo}_6$ octahedra, which are covered by iodine ligands, contain only sulfur atoms.

To interpret our results, we schematically represent the structures of Fig. 1 in Fig. 2. In the representation of Fig. 2, we first lay down the molybdenum octahedra onto one of their faces, which is to be considered the projection plane. Next, we consider the position of ligands decorating all faces except those parallel to the projection plane. Of the six ligands, two triplets will form two equilateral triangles, which are rotated by 180° with respect to each other, in planes parallel to the projection plane. These triangles, with the corners corresponding to the ligand positions, are depicted in Fig. 2. Clearly, structures with $x=0, 1, 5, 6$ iodine atoms have only one structural isomer, which is labeled as I(0) in Figs. 1 and 2. Structures with $x=2, 3, 4$ iodine atoms have three structural isomers each. Our binding energy results in Fig. 2 suggest that the relative stability of these structural isomers can differ by up to $\approx 0.35$ eV. We find that the most stable isomer for each stoichiometry, which is marked by an underlined red label, also has the highest symmetry. Since the interiodine distance is maximized in the favored...
structures, energy stabilization of the symmetric structures can be understood in terms of reducing Coulomb repulsion.

B. Connection between building blocks in nanowires

In previous studies, both sulfur\textsuperscript{17,19,20} and iodine\textsuperscript{3,24} have been postulated to form connecting bridges between functionalized Mo\textsubscript{6} building blocks in Mo\textsubscript{6}S\textsubscript{9−}I\textsubscript{3−} nanowires. Furthermore, the stability of sulfur- and iodine-based connections has been claimed to be nearly the same.\textsuperscript{20} To identify the nature of energetically preferred bridges, we considered two structural isomers of infinite Mo\textsubscript{6}S\textsubscript{9−}I\textsubscript{3−} nanowires, one with iodine and the other with sulfur bridges connecting the Mo\textsubscript{6} based building blocks. A unit cell of the optimized structures, containing 30 atoms, is shown in Fig. 3. We performed a global structure optimization, including the relaxation of the unit cell size, and found the nanowire connected with sulfur bridges to be energetically more stable by 0.65 eV per 30 atoms, providing further support for the presence of sulfur bridges.

C. Elastic properties of nanowires

In bundles of nanowires, the Young’s modulus can be determined from the stress-strain ratio in the wire direction. Experimental observations\textsuperscript{10} of high Young’s modulus values near 420 GPa in Mo\textsubscript{12}S\textsubscript{9}I\textsubscript{9} and Mo\textsubscript{12}S\textsubscript{6}I\textsubscript{12} suggest that these nanowires should be very rigid in the axial direction. To explain this high rigidity, the bistable S\textsubscript{3} bridges,\textsuperscript{19,25} connecting the Mo-based building blocks, were postulated to contain one extra atom in the middle.\textsuperscript{10,24} To understand the difference between the S\textsubscript{3} and S\textsubscript{4} bridges in terms of axial rigidity, we determined the stability of Mo\textsubscript{12}S\textsubscript{9}I\textsubscript{9} and Mo\textsubscript{12}S\textsubscript{6}I\textsubscript{12} nanowires. The main difference between the compounds is an additional S atom in (b) inserted inside each of the S\textsubscript{3} bridges in (a). E denotes the total energy relative to the optimum structure and a is the lattice constant. The dashed lines are guides to the eye, connecting the data points. Quadratic fits to the data points near the equilibrium, which is related to the axial rigidity, are given by the solid lines.

Figs. 4(a) and 4(b). By using the quadratic fits of Fig. 4, we can calculate the Young’s modulus as \(Y=k(a_{eq}/A)\), where \(a_{eq}\) is the equilibrium lattice constant and \(A\) is the cross section of the nanowire. The cross-section area per nanowire in an infinite bundle, where the interwire distance has been optimized\textsuperscript{25} to be 9.4 Å, is \(A=76.5\ \text{Å}^2\). This allows us to determine the Young’s modulus of Mo\textsubscript{12}S\textsubscript{9}I\textsubscript{9} with S\textsubscript{3} bridges as \(Y=99\ \text{GPa}\) and that of Mo\textsubscript{12}S\textsubscript{11}I\textsubscript{9} with S\textsubscript{4} bridges as \(Y=109\ \text{GPa}\). Thus, we conclude that the central atom in the S\textsubscript{4} bridges does not necessarily increase the axial rigidity of the nanowires.

Our results are well within the wide range of reported theoretical and experimental values of the Young’s modulus in Mo\textsubscript{12}S\textsubscript{9}I\textsubscript{9} nanowires, with calculated data being generally much softer than the observed values\textsuperscript{10,20,25} The calculated value\textsuperscript{30} \(Y=45\ \text{GPa}\) in Mo\textsubscript{12}S\textsubscript{9}I\textsubscript{12} nanowires is much smaller than the other reported theoretical values,\textsuperscript{20} which are \(Y=82\ \text{GPa}\) and \(Y=94\ \text{GPa}\) in this system, which contains bistable S\textsubscript{3} bridge connectors, and the Y=114 GPa value in Mo\textsubscript{12}S\textsubscript{11}I\textsubscript{9} nanowires with S\textsubscript{4} bridges.\textsuperscript{20} An even larger value \(Y=320\ \text{GPa}\) has been predicted for Mo\textsubscript{6}S\textsubscript{9} nanowires.\textsuperscript{36} By comparing all available data, we conclude that the Young’s modulus may sensitively depend on the stoichiometry.

D. Compositional ordering and phase separation in nanowires

Since the synthesis of Mo\textsubscript{6}S\textsubscript{9}I\textsubscript{9} nanowires occurs in a single-step reaction directly from the elements,\textsuperscript{22} we explore the intriguing possibility of forming nanowires with an arbitrary iodine concentration. To account for phase separation, which may be expected in this case, we consider coexistence of domains with different compositions. In the simplest scenario, we consider domains with only two different compositions, which are identified by the iodine concentrations \(x_1\) and \(x_2\). Our objective is to determine the most stable domain structure for Mo\textsubscript{6}S\textsubscript{9}I\textsubscript{9} nanowires with an arbitrary value of the average iodine concentration (\(\langle x \rangle\)).
Before addressing inhomogeneous nanowires, we first identify the most stable structure of homogeneous nanowires. We identified the optimum geometry and binding energy of all nanowires formed with any of the building blocks depicted in Figs. 1 and 2, considering the possibility of parallel and antiparallel alignments of asymmetric building blocks along the nanowire and also the possibility of the bistable sulfur bridges being short or long. As suggested earlier, the most stable structural isomers in the infinite systems, which are depicted in Fig. 5, may deviate from those for the finite building blocks. The binding energy $E_b$ of the most stable structural isomer, which is given per unit cell with respect to isolated atoms, is indicated by the data points in Fig. 6.

To better distinguish which structures are more stable than would be expected for a mixture of noninteracting ligands randomly arranged along the nanowire, in Fig. 6b, we show the energy difference between the optimized uniform systems and the expectation value $\langle E_b \rangle$. The higher-than-average stability of nanowires with $x=3$ suggests the corresponding stoichiometry to be likely present in one of the components in the case of phase separation. On the other hand, we are unlikely to encounter dominant phases with $x=1$ or $x=5$.

Next, we consider a nanowire with the Mo$_6$S$_9$I$_x$ average composition which separates into two domains. We distinguish the first domain, 1, with the Mo$_6$S$_9$I$_x$ composition and length $L_1$, from a second domain, 2, with the Mo$_6$S$_9$I$_x$ composition and length $L_2$. The lengths of the domains are trivially related by $L_1 x_1 + L_2 x_2 = (L_1 + L_2) \langle x \rangle$. On...
In the first study, we consider an infinitely long Mo₆S₃I₆ nanowire as the semi-infinite leads. The quantum conductance of this system within the Landauer–Büttiker formalism.

In the following, we will consider the optimized, frozen structure of infinitely long and of finite nanowires sandwiched between gold leads and determine the quantum conductance of this system within the Landauer–Büttiker formalism.

E. Quantum transport in nanowires

One of the most attractive features of Mo₆S₉—I₉ nanowires is the presence of S₃ bridges, which are known to form well-defined, stable bonds to Au surfaces. We will calculate quantum conductance in nanowires with the Mo₆S₄.5I₄.5 stoichiometry since Mo₆S₉—I₉ nanowires do not readily attach to Au electrodes. The same Mo₆S₄.5I₄.5 average stoichiometry can be achieved by periodically alternating the A and B domains containing two Mo₆ octahedra, which are labeled A₂ and B₂ in Fig. 7(b). The decrease in stability with respect to the structure of Fig. 7(a), which is reflected in the positive value of the energy cost \( \Delta E \), indicates that the creation of additional domain walls is energetically unfavorable. This finding is further supported by an even larger value of \( \Delta E \) in the structure of Fig. 7(c), where the number of domain walls has doubled with respect to Fig. 7(b). The value of \( \Delta E \) for the system of Fig. 7(e) is not twice the value for the system of Fig. 7(b) since the local atomic arrangement near the \((A_1, B_1)\) domain boundary differs from that near the \((A_2, B_2)\) domain boundary.

In our simple energy estimates underlying Figs. 6(c) and 6(d), we ignored the energy associated with forming domain wall boundaries between regions with different compositions. In Fig. 7, we investigate the energy cost of domain wall boundaries in Mo₆S₉—I₉ nanowires with \( \langle x \rangle =4.5 \), which is addressed in Fig. 6(d). Those results suggest that the nanowire will be most stable when separating into domains A with the Mo₆S₃I₃ composition and domains B with the Mo₆S₄.5I₄.5 composition. To maintain the average stoichiometry, the size of the A and B domains must be equal.

The reference structure of an infinite Mo₆S₄.5I₄.5 nanowire, which is depicted in Fig. 7(a), contains a single domain of phase A, which is separated by a domain wall from a single domain of phase B. As suggested in Figs. 4(a) and 5, the most stable structures of phases A and B, which are labeled \( A_c \) and \( B_c \) in Fig. 7(a), exhibit an alternating sequence of short and long sulfur bridges. Figure 4(a) also suggests that in phase A, the orientation of the I(3c) building blocks, which are defined in Fig. 1, should alternate, as indicated by the arrows in Fig. 7(a).

Next, we study the quantum conductance of a finite Mo₆S₄.5I₄.5 nanowire segment sandwiched between Au(111) surfaces as “ideal” leads, which is shown in Fig. 9(a). We selected Au(111) leads since gold forms stable covalent bonds to Au surfaces.
The filling of the conductance dip of the contact with gold does not significantly change the Fermi energy occurs at the same energy just above the Fermi level of the infinite nanowire and the sandwiched nanowire structures and gold. The fact that the dip in the conductance is caused by the reflection at the Fermi level of the gold leads. The energy dependence of the conductance quantum $G_0$, which was calculated at zero bias by using a nonequilibrium Green function formalism, indicates that the conductance reduction at the interface between Mo$_6$S$_{4.5}$I$_{4.5}$ nanowires and gold to be very small. This is also likely to hold true for other Mo$_6$S$_x$I$_{x}$ nanowires with a different stoichiometry as long as the Mo-based building blocks are connected by sulfur bridges. Also, the delocalization of conduction electrons within the Mo$_6$ octahedra should contribute to an excellent electrical conductance behavior of the nanowires independent of the stoichiometry.

IV. SUMMARY AND CONCLUSIONS

We used $ab$ initio calculations to study the compositional ordering and quantum transport in Mo$_6$S$_{x}$I$_{x}$ nanowires. The skeleton of these nanowires consists of Mo octahedra, which are functionalized by S and I adsorbates and connected by flexible S$_3$ bridges. The optimum geometries and relative stabilities at different compositions are determined by using density functional theory. We find nanowires with $x=3$ to be particularly stable. Nanowires with other compositions are likely to phase separate into iodine-rich and iodine-depleted domains, some of which should have the Mo$_6$S$_{3.5}$I$_{2.5}$ stoichiometry. Our transport calculations, which are based on the non-equilibrium Green’s function formalism, indicate that the nanowires are metallic independent of composition and exhibit a quantum conductance of $G=3G_0$ with the three conductance channels involving the S$_3$ bridges.
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