Nanowire Gold Chains: Formation Mechanisms and Conductance

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Abstract

Structural transformations, electronic spectra and ballistic transport in pulled gold nanowires are investigated with ab initio simulations, and correlated with recent measurements. Strain-induced yield of an initial double-strand wire results first in formation of a bent-chain which transforms upon further elongation to a linear atomic chain exhibiting dimerized atomic configurations. These structures are stabilized by directional local bonding with spd-hybridization. The conductance of the initial double-stranded contact is close to $2(2e^2/h) \equiv 2g_0$ and it drops sharply to $1g_0$ during the transformation to a single chain, exhibiting subsequently a $\sim1g_0$ plateau extending over an elongation well above typical Au-Au distances.

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Generation of nanometer-scale crystalline wires (NWs) through elongation of materials’ contacts had been predicted via early molecular dynamics simulations [1], and their mechanical, structural, and electrical properties have been the subject of intensive investigations [2] owing to increasing basic and technological interest in such NWs. Most recently [3] high-resolution electron microscope (HRTEM) images, recorded during retraction of a tip from a gold surface, portrayed the development of a sequence of crystalline NW structures made of parallel atomic strands oriented along the NW axis, with the number of strands decreasing one-by-one culminating in an one-atom wide and four-atom long linear chain of Au atoms [3,4]. Furthermore, the simultaneously measured conductance revealed [3] a staircase of quantized values (close to integer multiples of the conductance quantum \( g_0 = 2e^2/h \)) with the disappearance of each atomic strand, coinciding at the final pulling stages with an approximate unit \( g_0 \) drop in the measured conductance. These experiments stimulated recent electronic structure calculations pertaining to single-chains of gold atoms [5–8].

Aiming at elucidation of the atomic-scale structural evolution and transformation mechanisms, and of bonding and transport characteristics at the ultimate stages of elongation of gold NWs, we report here results from large-scale \( \text{ab initio} \) density functional simulations [9,10] in conjunction with conductance calculations [11]. Our findings reveal that the formation mechanism of a four-atom long single chain NW, generated through straining of a double-strand (ds) wire (see bottom left configuration in Fig. 1a), involves stress accumulation followed by eventual yield of one of the atomic strands, with the consequent atomic rearrangement resulting first in a (lower-energy) bent-chain (bc) configuration (top left configuration in Fig. 1a). The yield event is accompanied by a significant decrease in the pulling force and a sharp drop in the conductance to \(~1g_0\) (see top in Fig. 1a). Further separation of the two electrodes results in a transformation to a linear-chain (lc) structure (see right configuration in Fig. 1a), with continued elongation leading to formation of dimerized configurations. Initial dimerization develops between the inner atoms of the wire (i.e. inner-dimerization, id), transforming at a later stage to one where each of the inner atoms pairs with an end-atom of the chain (i.e. end-atom dimerization, ed). During the ds→bc→lc evolution the conductance exhibits a ~\(1g_0\) extended (4 Å – 4.5 Å long) plateau (see Fig. 1a). The optimal structures determined here are stabilized by directional local bonding involving \(s, p\) and \(d\) hybridization near the Fermi energy, and they are found to be energetically favorable to certain suggested alternative structural models [7].

We start from a relaxed ds wire configuration with the distance between the two outermost layers of the opposing Au electrodes held at \( L = 11.5 \) Å; each of the electrodes is composed of 29 atoms arranged in 3 layers with face-centered-cubic (110) stacking in the \( z\)-direction (along the wire) and exposing \{100\} and \{111\} side facets. This crystallographic orientation, and the subsequent elongation process and conductance characteristics discussed below, correspond to experiments discussed in Ref. 3 and described in Fig. 3 of that paper, where HRTEM and conductance measurements pertaining to gold nanowires created via controlled elongation of the contact between a tip and a (110) facet of a gold island are displayed. Note that this experiment is distinctly different from the one corresponding to Fig. 4 of Ref. 3, which pertains to a wire formed through (spontaneous) thinning of a ”nanobridge” connecting across a hole formed in a gold film by intense electron bombardment (in particular, unusually large interatomic distances of up to 3.5 Å – 4 Å were reported in Ref. 3 for the latter case, and \textit{not} for the tip-pulling experiments which are the focus of
our study).

In this initial configuration the 2-atom strands are parallel to each other, with almost equal inter- and intra-strand separations, \(d_{\text{intra}}(1', 2') = d_{\text{intra}}(1, 2) = 2.66 \, \text{Å} \) and \(d_{\text{inter}}(1', 1) = d_{\text{inter}}(2', 2) = 2.67 \, \text{Å} \) (see atom numbering in Fig. 1a), and the distance between the topmost (interfacial) facets of the opposing electrodes is \(d_{\text{el-el}} = 6.02 \, \text{Å} \). Note that all the distances involving atoms bridging the electrodes are smaller than the nn interatomic distance in bulk gold (2.885 Å), but larger than the bond-length of the free Au$_2$ dimer (2.48 Å). The calculated conductance \([11]\) of this configuration is 1.

Elongation of the wire is simulated through increasing the separation between the outermost layers of the opposing electrodes (where the atoms are held at their fcc lattice positions with a lattice constant of bulk gold, 4.08 Å), followed by full relaxation of the system after each elongation step. The total elongation simulated here is \(\Delta L = 6.5 \, \text{Å} \) (using elongation increments of \(0.25 \, \text{Å} \leq \delta L \leq 1 \, \text{Å} \), see Fig. 1a), and we found that structural changes in response to increments in \(L \) involve mainly atoms forming the connective wire bridging the electrodes.

\textit{ds→bc transformation} (\(L \leq 13.3 \, \text{Å} \)). Initial elongation results in higher-energy strained configurations with the pulling forces rising to \(\sim 4 \, \text{nN} \) (corresponding to the elongation increment from \(L = 12.3 \, \text{Å} \) to 12.6 Å, see Fig. 1a), and it is accompanied by a gradual (small) decrease of the conductance to \(G = 1.68g_0 \) in the highly strained ds configuration shown at the bottom left in Fig. 1a (corresponding to \(L = 12.6 \, \text{Å} \) with \(d_{\text{el-el}} = 6.95 \, \text{Å} \)).

For all the ds configurations the ballistic electron transport involves mainly two conductance eigenchannels (CCs), with the total conductance \(G = g_0 \sum_n |\tau_n|^2 \), where \(0 \leq |\tau_n|^2 \leq 1 \) is the transmission probability of the \(n\)th eigenchannel; for the initial ds configuration \(|\tau_1|^2 = 0.99, |\tau_2|^2 = 0.76 \), and for the highly-strained one \(|\tau_1|^2 = 0.97, |\tau_2|^2 = 0.70 \). The CCs are determined by quantization of the electron motion transverse to the propagation direction (\(z\)), due to the lateral confinement by the effective wire potential \([10],[11]\). Each of the transmitted CCs is found to be delocalized over the two atomic strands with the first CC being nodeless, and the second having a nodal plane normal to the plane defined by the two strands and bisecting the interstrand Au-Au bonds (see Fig. 2a); the delocalized nature of the CCs contrasts the conjecture \([3]\) that in such multi-strand NWs each of the two strands and bisecting the interstrand Au-Au bonds (see Fig. 2a); the delocalized nature of the CCs contrasts the conjecture \([3]\) that in such multi-strand NWs each of the channels is associated with (and is confined about) an individual atomic strand implying two independent CCs connected in parallel to the electrodes.

The ds→bc elongation stage culminates in breaking of one of the strands, accompanied by displacements of each of the end atoms of the broken strand (1' and 2' in Fig. 1a) to the center of the underlying (110) rectangular facet of the corresponding electrode, yielding a lower-energy bc configuration, with a concomitant sharp drop in the conductance to 1 \(g_0 \) (see Fig. 1a) involving a single CC. In the relaxed bc configuration (top left structure in Fig. 1a) the end-to-end wire length \(l_{\text{ee}} \equiv d(1', 2') = 5.12 \, \text{Å} \), the distance between an interior atom to an nn end-atom of the wire \(d_{\text{ie}} = d(1, 1') = d(2, 2') = 2.62 \, \text{Å} \), the bond length between the internal atoms of the wire \(d_{\text{ii}} = d(1, 2) = 2.56 \, \text{Å} \), and the bond angle \(\angle(1', 1, 2) = 119^\circ \).

\textit{bc→lc transformation} (13.3 Å \(\leq L \leq 16.3 \, \text{Å} \)). During subsequent elongation, requiring initially a small pulling force (\(\sim 0.8 \, \text{nN} \), corresponding to the interval between \(L = 13.3 \, \text{Å} \) and \(L = 13.8 \, \text{Å} \), the bc wire straightens gradually resulting eventually (see right configuration in Fig. 1a) in a linear chain at \(L = 16.3 \, \text{Å} \) \([13]\). The bc→lc transformation spans an elongation range \(\Delta L(\text{bc} \rightarrow \text{lc}) = 3.0 \, \text{Å} \), during which the conductance decreases only by
about 10% (from 1\(g_0\) for the initial bc configuration to 0.87\(g_0\) for the lc one at \(L = 16.3\ \text{Å}\)).

In light of a recent report pertaining to alternative structures for single-chain gold nanowires [4] we have explored such configurational isomers during the bc stage, with two of them shown in Fig. 1b; a planar 4-atom rhombohedral (rh) arrangement at \(L = 13.3\ \text{Å}\) and a ”zig-zag” (zz) structure at \(L = 14.8\ \text{Å}\). Energetically, these (relaxed) structural isomers are found to be local minima with higher energies (and slightly lower conductance) than the corresponding bc configurations (see Fig. 1a). The zz isomer and bc structure (as well as the lc) become approximately degenerate at \(L = 15.8\ \text{Å}\), and upon further elongation (i.e. for \(L = 16.3\ \text{Å}\)) both the zz and the bc convert to a linear chain. Note that although all these isomers (rh, zz, bc, lc) are found to be local minima for a free Au\(_4\) cluster, the energetic ordering of structural isomers observed here for the four-atom NW cannot be deduced from that of the free cluster [14].

\text{lc→breaking (}L \geq 16.3\ \text{Å).} With continued pulling the lc wire shows a tendency toward dimerization. At first (for \(16.3 \leq L \leq 17.3\ \text{Å}\)) the only stable structures correspond to internal dimerization (id) of the wire, with \(d_{ii} < d_{ie}[14]\). At the start of this elongation interval the conductance decreases only slightly, with a marked drop at \(L = 17.3\ \text{Å}\). However, starting at \(L = 17.3\ \text{Å}\) an energetically competitive dimerization mode of the lc wire emerges (being essentially degenerate with the id structure at 17.3 Å) where \(d_{ii} > d_{ie}[14]\), with the conductance of this end-dimerized (ed) structure being \(1g_0\). We note here (see Fig. 1a) the markedly higher conductance of the ed structure (\(G = 1g_0\)) compared to that of the corresponding id chain [17]. Such end-dimerized structures [4] are energetically favored for the rest of the elongation process (that is for \(L > 17.3\ \text{Å}\)) [18]. The force required for elongation during the end-dimerization stage is rather small (i.e. \(\sim 0.3\ \text{nN}\) in the interval \(17.6\ \text{Å} \leq L \leq 18\ \text{Å}\)), and the conductance of the wire decreases sharply as eventual breaking is approached.

Throughout the structural evolution the electronic spectrum in the wire region is characterized by a dominant contribution of atomic \(d\) orbitals in the energy range \(E_F - 4.5\ \text{eV} \leq E \leq E_F - 1\ \text{eV}\), with \(s, p\), and \(spd\) hybrids contributing at energies above and below this range. Examination of the local densities of states reveals that the main variations in the spectrum in response to the mechanical elongation occur predominantly in the interelectrode spatial region (the wire atoms, and the electrode atoms bound directly to them), involving mainly states in the vicinity of \(E_F\).

To illustrate the nature of these states and their high sensitivity to structural variations we examine, for selected atomic configurations developed during the elongation process, orbital images (Fig. 2(b-d)) and their angular-momentum decompositions about the wire atoms, corresponding to electronic states near \(E_F\) (i.e. highest occupied molecular orbitals, HOMO\((j)\), with the index \(j = -1, -2\) corresponding to the next-to-highest occupied orbitals in descending order). We observe that for the ds structure (see Fig. 2b and the configuration shown at the bottom left in Fig. 1a) the HOMO is of predominant \(d_{xz}\) character (\(p_{x}^{0.2}d_{xz}^{0.76}\), here and in the following only the dominant \(m\)-components of \(p\) and \(d\)-characters are given) and the HOMO(-1) is of strong \(sp_z\) character (\(s^{0.34}p_{z}^{0.65}d_{2z}^{0.12}\)) on the strand atoms. These states evolve after the ds→bc transformation (see top left configuration in Fig. 1a) into a HOMO with \(s^{0.45}p_{x}^{0.50}\) (\(p_{x}^{0.25}d_{xz}^{0.32}\)) on inner-(end-) atoms, and a HOMO(-1) with an almost pure (tilted) \(d_{xz}\) character on the inner-atom (\(p_{x}^{0.03}d_{z}^{0.9}\)) and a (\(s^{0.5}p_{x}^{0.08}d_{xz}^{0.32}\)) hybrid.
on the end-atoms of the bent-chain (Fig. 2c).

The structural evolution during the bc→lc stage and the formation of dimerized configurations of the lc are accompanied by reordering of the orbitals near $E_F$ with the HOMO orbital on the inner atoms of the wire acquiring a predominant $p_{x,0.03}^0d_{xz,0.95}^0$ character (see e.g. Fig. 2d corresponding to the ed configuration); as evident the $d_{xz}$ components on the two inner atoms of the ed wire combine locally in an antibonding manner, while in the (lower-energy) HOMO(-1) orbital (not shown) they are in a local bonding orientation with respect to each other. The HOMO(-2) orbital (Fig. 2d) of the ed configuration is characterized by a strong $s$ character on the inner-atoms ($s^{0.86}p_{z,0.11}^{0.06}d_{xz,0.03}^{0.48}$) combining to form a $\sigma$-like local bond, and an $sd$ hybridization on the end-atoms of the chain ($s^{0.48}p_{x,0.06}^{0.06}d_{xz,2,y}^{0.46}$).

The above hybridization patterns and in particular the strong contribution from $d$-orbitals to directional covalent-like bonding characteristics in the (interelectrode) wire region, underlie and facilitate the structural transformation mechanism described by us, via stabilization of the sequence of strained atomic configurations which evolve in the elongation process. Consequently, formation of such (several atom long) single-chain nanostructures, reflected in an extended conductance plateau (with close to unit conductance) before breaking may not be found for materials where the above bonding patterns do not occur; indeed extended single-chains were not observed (theoretically and experimentally) for a simple metal contact (e.g. sodium).

Finally, we remark that the investigations presented here, which deepen our insights into the structure, formation mechanism, and conductance of atomic double-strand and single-strand nanocontacts between gold electrodes, pertain to the type of tip-pulling experiments reported in the first part of Ref. 3 (see Fig. 3 in Ref. 3), and they are not aimed at explaining the extraordinary stability of monoatomic thick wires bridging two sections of a suspended thin gold film, where interatomic distances up to 3.5 Å – 4 Å were reported from HRTEM images (see the second part of Ref. 3, particularly Fig. 4 therein). Indeed, the formation of wires in the latter experiments involves an initial intense electron bombardment to perforate holes in the film and subsequent thinning of the formed "nanobridges" driven by stress and strain relaxation processes; additionally, the nature of such experiments differs greatly from the controlled tip-pulling experiments, on which we focus here. We remark that none of the theoretical studies reported to date have been able to consistently explain the abovementioned anomalously long interatomic distances in the nanobridges, indicating that new theoretical considerations are needed, including examinations of possible effects caused by light impurity atoms, which while affecting the structure of the nanowire may not have enough contrast to be visible in HRTEM images.

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FIGURES

FIG. 1. (a) Energies ($\Delta E$, in unit of eV plotted at the bottom, relative to the initial ds configuration at $L = 11.5$ Å) and conductances ($G$, in unit of $g_0$, plotted at the top) of Au NWs versus the distance between the outermost layers of the opposing electrodes, $L$; the double-strand (ds, squares), bent-chain (bc, triangles), and linear-chain (lc, circles) intervals are marked at the top. The values for the rhombic (rh) isomer at $L = 13.3$ Å and for the zig-zag (zz) isomers at $L = 14.8$ Å and $15.8$ Å are marked by crosses, and those for the end-dimer configurations at $L = 17.3$ Å, $17.6$ Å and $18$ Å are depicted by stars. The elongation force between consecutive structures may be estimated by the corresponding slope $\Delta E/\Delta L$. The atomic configurations (with atom indices) shown as insets to (a) correspond to the ds (left, bottom), bc (left, top), and lc (right) structures at $L = 12.6$ Å, $13.3$ Å and $16.3$ Å respectively. (b) atomic configurations for the rh isomer at $L = 13.3$ Å ($d(1,2) = 2.76$ Å, $d(2,3) = 2.59$ Å, and $\angle (1,2,4) = 124^\circ$), and for the zz isomer at $L = 14.8$ Å ($d(1,2) = d(3,4) = 2.55$ Å, $d(2,3) = 2.52$ Å and $\angle (1,2,3) = 119^\circ$).

FIG. 2 (color) (a) Iso-surface images of the magnitudes of the first ($0.97 g_0$, top) and second ($0.7 g_0$, bottom) transmitted eigenchannels for the highly-strained ds configuration (at $L = 12.6$ Å). (b and c) HOMO (top) and HOMO(-1) (bottom) orbitals corresponding to the highly-strained ds NW (in b) and to the bc configuration at $L = 13.3$ Å (in c). (d) HOMO (top) and HOMO(-2) (bottom) orbitals for the ed configuration at $L = 17.3$ Å. In (a-d) Au atoms are depicted by red spheres. In (a) we display the entire atomic system including parts of the jellium-slab continuations of the electrodes (used in the conductance calculations), and in (b-d) we focus on the vicinity of the nanowires. The viewing orientation was chosen in each case to enhance visualization of the orbital characters on the wire atoms.
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For a relaxed longer ds wire (i.e. two 4-atom-long strands with \(d_{\text{inter}} = 2.59 \, \text{Å}, d_{\text{intra}} = 2.73 \, \text{Å}, \text{and } d_{\text{el-el}} = 11.73 \, \text{Å}\)), we obtained \(G = 1.97 g_0\).

In the lc configuration at \(L = 16.3 \, \text{Å} \ell_{\text{ee}} = 7.94 \, \text{Å}, d_{\text{ie}} = 2.66 \, \text{Å}, \text{and } d_{\text{ii}} = 2.62 \, \text{Å}\).

The same LDA calculations (Ref. 9) for the free Au\(_4\) cluster show that the ground state is a planar rhombus (rh) with \(d(1, 2) = 2.70 \, \text{Å} \text{ and } \angle(1, 2, 4) = 121^\circ\). The zz isomer with \(d(1, 2) = d(3, 4) = 2.55 \, \text{Å}, d(2, 3) = 2.60 \, \text{Å} \text{ and } \angle(1, 2, 3) = 130^\circ\) (see atom numbering in Fig. 1b for rh and zz) is of higher energy \((\Delta E = 0.84 \, \text{eV})\), and the lc isomer, with \(d(1, 2) = d(3, 4) = 2.52 \, \text{Å} \text{ and } d(2, 3) = 2.59 \, \text{Å}\), is of even higher energy \((\Delta E = 1.34 \, \text{eV})\). A bc isomer \(d(1, 2) = d(3, 4) = 2.51 \, \text{Å}, d(2, 3) = 2.61 \, \text{Å}, \text{and } \angle(1, 2, 3) = 126^\circ\) is found to be the highest in energy \((\Delta E = 1.40 \, \text{eV})\).

For \(L = 16.3 \, \text{Å}\) see Ref. 12, and for \(L = 17.3 \, \text{Å} \ell_{\text{ee}} = 8.82 \, \text{Å}, d_{\text{ii}} = 2.68 \, \text{Å}, \text{and } d_{\text{ie}} = 3.07 \, \text{Å}\).

For the ed structure at \(L = 17.3 \, \text{Å} \ell_{\text{ee}} = 8.75 \, \text{Å}, d_{\text{ii}} = 3.31 \, \text{Å}, \text{and } d_{\text{ie}} = 2.72 \, \text{Å}\).

The significantly smaller conductance of the id configuration at \(L = 17.3 \, \text{Å}\) (see Fig. 1a) is caused by narrowing of the potential profile in the regions between the internal dimer atoms and the end-atoms of the chain (see Fig. 4a in Ref. 10), with the consequent reduced coupling between the inner dimer atoms and the electrodes, resulting in enhanced back-scattering of the incident electron from these ”bottle-neck” regions. Note that at finite temperature fluctuations between the essentially degenerate id and ed structures may occur leading to sizable noise in the measured conductance \((G \sim 0.6 – 1 \, g_0)\) at the final stages of elongation.

At \(L = 17.6 \, \text{Å} \ell_{\text{ee}} = 9.34 \, \text{Å}, d_{\text{ii}} = 4.24 \, \text{Å}, d_{\text{ie}} = 2.55 \, \text{Å}, \text{and at } L = 18 \, \text{Å} \ell_{\text{ee}} = 9.81 \, \text{Å}, d_{\text{ii}} = 4.75 \, \text{Å}, \text{and } d_{\text{ie}} = 2.53 \, \text{Å}\).

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In ref. 7 it was suggested that experimentally observed linear wires with long interatomic distances would in fact consist of spinning ”zigzag” structures having typical Au-Au nearest-neighbor distances, but with only the atoms on the rotation axis visible in HRTEM. However, in such structures even the spinning off-axis atoms should generate enough contrast to be clearly visible for imaging (D. Ugarte, private communication).

For instance, while it is well known that oxygen does not adsorb molecularly on bulk gold, it may interact more strongly with the formed nanobridges of the film, and may even dissociate due to heating/strain effects in the film. Atomic oxygen binds strongly on small gold clusters with typical O-Au distance of 1.9 – 2.1 Å (H. Håkkinen, unpublished data). Linear chains of alternating Au and O atoms (provided that they would be stable as suspended chains) would thus have Au-Au distances of \(\approx 4 \, \text{Å}\). For a discussion of related chemical adsorption effects on the structure and electric transport properties of gold nanowires see ref. 10.
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