Helical [110] Gold Nanowires Make Longer Linear Atomic Chains

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Quantum mechanical molecular dynamics shows that gold nanowires formed along the [110] direction reconstruct upon stress to form helical nanowires. The mechanism for this formation is discussed. These helical nanowires evolve on stretching to form linear atomic chains. Because helical nanowires do not form symmetrical tips, a requirement to stop the growth of atomic chains, these nanowires produce longer atomic chains than other nanowires. These results are obtained resorting to the use of tight-binding molecular dynamics and *ab initio* electronic structure calculations.

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Metal nanowires (NWs) in general and gold NWs in particular have recently been the subject of intense theoretical and experimental research. This interest has mainly risen after the early molecular description of the formation of thin NWs from the elongation of a metal tip in contact with a gold surface was evidenced [1], together with the fact that very thin metal NWs were shown to be stable structures [2]. These NWs can be grown in different crystallographic directions. NWs show quantized conductance in units of $2e^2/h$, and single chains of gold atoms were confirmed to have one unit of conductance [2]. Many techniques such as pulling atoms with a scanning tunneling tip (STM) [1,3–5], separating two metals with a mechanically controllable breaking junction [6,7], or by producing holes in a gold thin foil with a high resolution transmission electron microscope [8–10] were used to produce surprisingly stable chains of atoms, with the formation of metallic wires, one atom thick and a few atoms long. These experiments have motivated theoretical studies attempting to understand the formation and evolution on one atom thick gold NWs [11–14].

Experiments performed on NWs synthesized by electron beam irradiation technique have shown that gold NWs formed along the [110] direction become helical when the NWs are sufficiently thin [15] and presenting a (111) outermost shell. Moreover, platinum NWs were also reported to produce helical structures [16]. Lead and aluminum helical NWs have been theoretically predicted in computer simulations [17]. Density functional theory calculations showed that helical NWs with magic numbers were stable [18]. Beyond these works on the stability of helical NWs, few other contributions on the question of mechanisms for the helical formation in these NWs are available at present. Recently, Iguchi *et al.* [19] proposed a mechanism for helical NW formation. It is a two stage model which uses an additional line of atoms attached to the otherwise perfect [110] NW that upon reconstruction shows the helicity being formed using tight-binding molecular dynamics (TBMD). While it is a very interesting idea, the aggregation of a line of atoms seems difficult to obtain in experiments.

In the present Letter we first present an explanation for the formation of helical structures. Computer molecular dynamics simulations seem to indicate that an intrinsic mechanism is responsible for the helical formation in [110] gold NWs under stress. Second, our study of this helical NW under tension allows us to identify why it makes a longer linear atomic chain (LAC) than nonhelical NWs. Finally, we use *ab initio* calculations to study the NW obtained from the TBMD simulations at stages close to rupture and compare LAC interatomic distances obtained with both methods. Furthermore, we investigate the electronic structure of the NW close to rupture.

In the first part of the present study we resort to MD simulations with a tight-binding parametrization [20] that have been used to study bulk and liquid gold [21] and have been successfully used to study gold nanowires [11,12,19]. The simulation protocol for the dynamical evolution of the NW under stress is as follows: (i) Simulation starts with 85 atoms packed in 10 planes of alternating 8 and 9 atoms, oriented along the [110] growth direction. This initial configuration, assumed to be at 600 K, is then annealed to lower temperatures by 5000 MD steps (5 ps), which results in a cylindrical helical geometry with the surface atoms reconstructing into a densely packed structure; (ii) the wire is elongated by 0.4 Å; (iii) the temperature is increased up to 600 K; (iv) the system is annealed for 3000 MD steps (3 ps) decreasing the temperature to below 50 K. Steps (ii) –(iv) are repeated until rupture of the NW. This protocol was successfully used to study gold [11,12] and copper NWs [22].

The helical NWs analyzed in the experiments are structures under stress, which is a key factor to their formation. NWs grown in the [111] direction form straight wires and the reason is that they are composed of stacks of (111) planes perpendicular to the growth direction. The surface atoms from these planes reconstruct forming rings that compose the rounded surface of the cylindrical NWs, which is a {111} surface displaying hexagons with no chirality. On the other hand, NWs grown along the [110] direction have (111) planes that are at an angle with the NW direction. These planes are very compact with shorter

bonds than those from (110) planes, along the growth direction or perpendicular to it. When the NW is under tension along the [110] direction, the compact (111) planes relax to form rings, keeping registry of their initial angular arrangement. As a consequence the outermost shell that would otherwise expose facets reconstructs into a helical rounded {111} surface, which is the lowest free energy for gold. The first stage of the evolution of the NW is shown in Fig. 1, which presents the evolution of an fcc NW formed in the [110] direction. Before relaxation it exhibits {001} and {110} facets which after relaxation under MD become a rounded surface. The fcc structure is stressed along the axis direction by 2.6% of its bulk value. Figure 1 presents three views of the NW's structure to explain the mechanism of the formation of the helical structure, which is the result of the structural reconstruction. Figure 1(a) presents the initial structure with the (111) planes colored in blue so we can follow their evolution. The lines formed by the (111) atoms are at an angle of 54° with respect to the axis of the NW. They are responsible for the formation of the hexagons that form the {111} outer surface, and in trying to keep registry of this direction, they produce the helical line around the NW. Note that in the {001} facets the blue atoms from the (111) planes are lines perpendicular to the NW's axis, as can be seen in Fig. 1(a). Therefore these lines [the green and red lines in Fig. 1(b)] rearrange by slipping to accommodate the hexagonal formation to become {111} rounded surfaces that match the tilted (111) rings completing the helical formation. The process of helical formation also involves rounding the planar facets into ring-type structures [Fig. 1(c)] with atoms from the interior migrating to the outer surface to complement the formation of the {111} external surface but accompanied with formation of defects. The overall process of relaxation is the reconstruction towards a NW presenting a tilted {111} helical surface.

One interesting question is the further evolution of this helical NW under tension. Mechanochemistry, the ability of changing coordination numbers of atoms and therefore bonding properties, is a very interesting concept that gets more important in nanosystems, and gold is of particular interest since it forms one-dimensional LACs. Similar to the experiments where the NW is under tension, we study this evolution observing the structures and the forces supported by the NW as it is stretched. Figure 2 displays the force profile of the evolution of the NW. We observe that the force has a typical sawtooth behavior previously seen in other calculations and experiments. This behavior is due to the fact that the NW supports periods of tension without

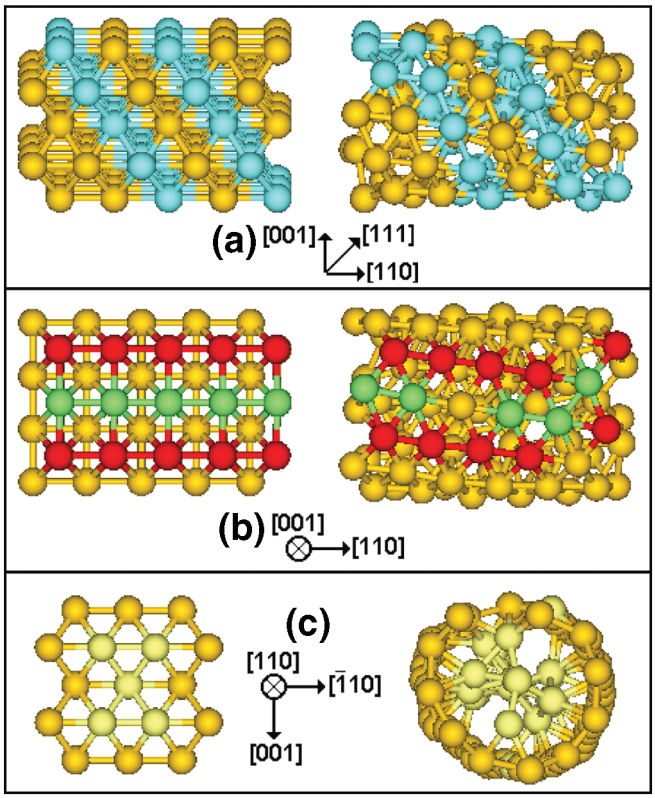

FIG. 1 (color). Evolution of the [110] fcc NW: Figures at the left are the fcc structure that, after relaxing under MD evolution, evolves to the structure in the right. Three views of this evolution are shown. (a) shows the (111) planes, (b) shows the {001} facet, and (c) shows a front view of the ring formation.

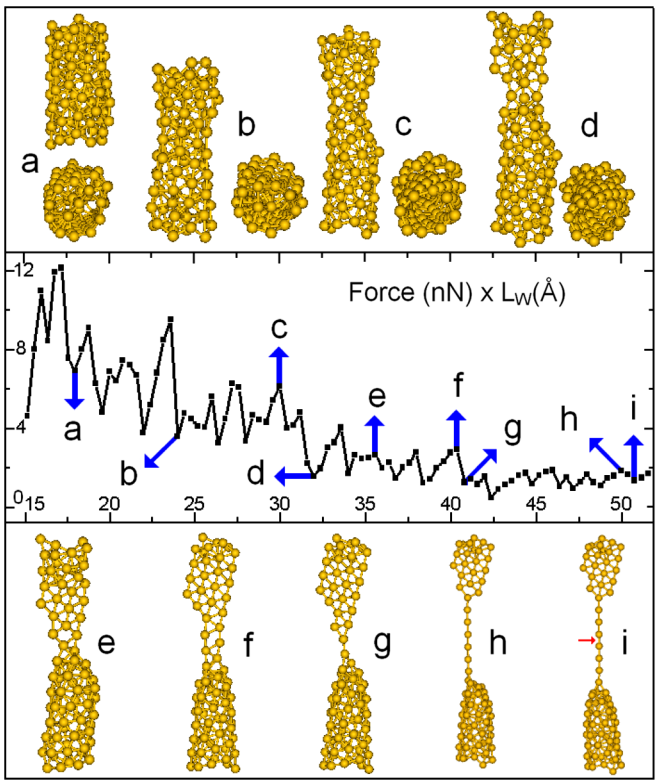

FIG. 2 (color online). TBMD calculated forces sustained by the [110] helical NW, as function of NWs elongation L_W, during its evolution until its rupture, along with selected stages of the NW's structure, representative of the evolution. The red (light gray) arrow indicates where the rupture occurs.

structural distortion that are the linear parts of the force profile, but at some stages reconstructions occur in order to lower tension. In Fig. 2 selected stages of the NW's evolution are displayed and presented with two views of the structure. One displays the NW along its axis showing the formation of the one atom constriction and LAC and a front view where the helicity is evidenced. The helical formation continues during the whole evolution process, even after the one atom constriction which evolves into a LAC of atoms that at some stage ruptures. Similar simulations performed for copper NWs in the [110] direction did not evolve to helical structures [22], as reported also by Iguchi *et al.* [19].

Other important result consists in that helical [110] gold NWs form longer LACs than NWs grown in other directions and that are not helical. The reason for this is that helical structures favor the formation of tips with low symmetry, which provide a mechanochemical facility to break bonds and therefore produce longer LACs. Similar results were obtained when pulling the 7-1 structure proposed by Tosatti *et al.* [18], an intrinsic helical structure by construction.

The evolution of the NW under tension is depicted in Fig. 2. The structure in (a) is a rodlike helical structure, and its outer surface is a helical {111} rolled surface. As the NW is pulled, atoms from the interior move to the surface in order to fill defects that start to form, and the NW tends to become a hollow tube. In (b) tension starts to thin the NW as shown in (c), where a neck starts to develop and evolves in (d). The hollow NW restructures under tension differently than NWs that have planes of atoms perpendicular to the NW's axis. One of the tips (the upper one) starts to open its surface (e) to form a nanoribbon (NR) while the other tip continues helical. From (e) to (f) the NR evolves to a stair-type structure that further evolves into a one atom constriction (g), which in turn is the beginning of the LAC formation. In this helical structure both tips lack symmetry and therefore give atoms to form the LAC with 8 atoms from apex to apex. The upper tip in (g) is attached to two atoms while the lower tip is helical, and since it does not have perpendicular planes of atoms, tension is not evenly distributed between the tip bonds favoring the breaking of atomic bonds that add atoms into the LAC. Both tips, due to the lack of symmetry, contribute to the LAC formation and produce a longer LAC. Around the wire elongation $L_W = 50.8$ Å the helical lower tip becomes symmetrical with the apex atom attached to three other atoms that form the tip [stage (i)] favoring the rupture. The breaking force is 1.7 nN in agreement with experimental [23] and theoretical results [11].

To further understand the properties of this long LAC formation, we also studied the NW's final stages before rupture with *ab initio* electronic structure calculations using total energy density functional theory [24,25]. Calculations used the SIESTA code [26]. Details of the calculations are given in Ref. [12]. A norm-conserving Troullier-Martins pseudopotential [27] was used with generalized gradient approximation [28] for the exchange-correlation functional. Supercell was defined with periodic boundary conditions to define a chain geometry avoiding interaction between the NW and its images. A Brillouin zone sampling used 8 Monkhorst-Pack k points along the NW tube axis [29]. The NW obtained from the TBMD had the atomic positions relaxed until all force components were smaller than 0.01 eV/Å.

Figure 3 compares the final structure obtained in the TBMD simulation with the *ab initio* calculation. Interatomic distances in both calculations are indicated. Under tension both set of distances are rather similar. The *ab initio* LAC is 5% larger than the TBMD one. The *ab initio* calculated force is 2.2 nN, which is in good agreement with the TBMD value previously presented and with other *ab initio* calculations [12,23,30,31]. Both structures broke at the same bond. These results show that the TBMD calculation describes well the gold NW.

Using the electronic structure calculation of the final structure before rupture, we obtain the densities of states of selected atoms. Figure 4 presents the projected densities of states (PDOS) per orbital (s and d) for selected atoms shown at the top of the figure, those in red and numbered. On the left, PDOS of atoms 1, 2, and 3 are shown. The bulk DOS was superimposed on the PDOS of atom 1. Atom 1 is what can be called a "bulklike" atom, since it is far from the NW's tip; in fact, PDOS is rather similar to the bulk DOS. Although atom 1 is bulklike, its PDOS shift towards the Fermi energy (E_F) since it has only 6 near neighbors. Atom 2 is in the ribbon structure and also has 6 bonds; this structure is planar, and therefore bond angles are different from the case of atom 1. Atom 3 that is at the border of the

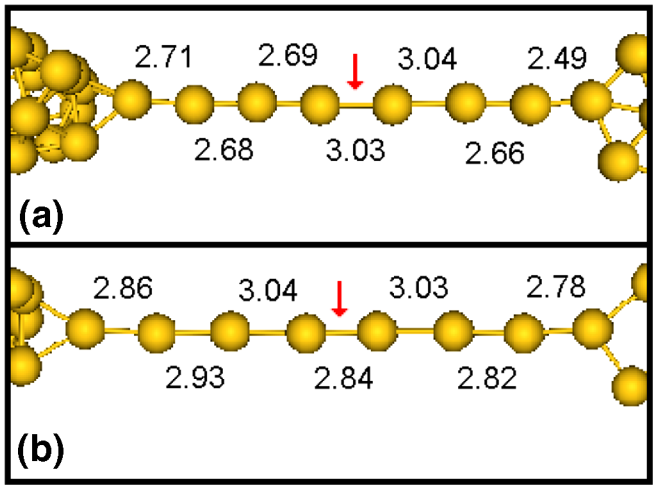

FIG. 3 (color online). TBMD and *ab initio* structures and distances prior to rupture of the NW. Interatomic distances are shown in (a) for the TBMD and (b) for the *ab initio* calculation. The arrows show the bond where rupture occurs.

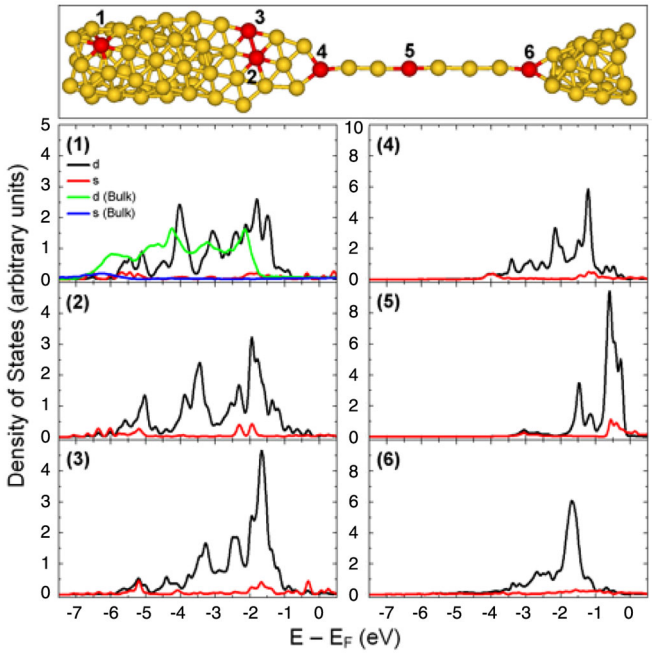

FIG. 4 (color online). Orbital projected density of states of selected atoms from the *ab initio* final structure. Selected atoms are shown in the structure above.

NR with 4 neighbors has its DOS peaking at about −1.6 eV consequence of the change in the coordination number. On the right of Fig. 4 the PDOS for LAC atom 5 and apex atoms 4 and 6 are displayed. As the coordination number goes down, the PDOS peaks closer to E_F. This is clearly seen in the case of atom 5, which has only two bonds with an angle of 180° between bonds. The helical NW with a long LAC of 8 atoms has electronic states strongly influenced by the coordination and bond angles of their atoms.

In conclusion, in this Letter we have discussed two important questions regarding thin gold [110] NWs. First, they intrinsically tend to become helical and this behavior is caused by the compact (111) planes forming an angle with the NW's direction. It is also shown that this helical formation of the NW is sustained even when it starts to further thin making necks. Second, the neck under tension evolves into a LAC that grows longer than NWs grown in other directions. This is again due to the helical structure of the tips that lack symmetry so the bonds near the tip break more easily than they would in a more symmetrical NW. Finally, we used *ab initio* calculations to corroborate our TBMD calculations with a discussion of the electronic states in the final stages of the evolution of the studied NW.

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