How Do Gold Nanowires Break?

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Suspended gold nanowires have recently been made in an ultrahigh vacuum and were imaged by electron microscopy. Using realistic molecular dynamics simulation, we study the mechanisms of formation, evolution, and breaking of these atomically thin Au nanowires under stress. We show how defects induce the formation of constrictions that eventually will form the one-atom chains. We find that these chains, before breaking, are five atoms long, which is in excellent agreement with experimental results. After the nanowire's rupture, we analyze the structure of the Au tip, which we believe will be universally present due to its highly symmetric nature.

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Miniaturization challenges science to understand the behavior of materials under circumstances other than those encountered in bulk solids. Gold nanowires suspended between electrodes have attracted a great deal of interest in the past few years, because of their great importance in fundamental physics as well as in technology, since miniaturization of devices needs metallic contacts. Au nanowires have been experimentally produced by contact of a metal surface with a scanning tunneling microscope [1–4] and also from thin films [5–7]. Surprises such as helical nanowire structures have been theoretically predicted [8] and experimentally observed [5] in gold. Under stress, these wires, before breaking, can get as thin as one-atom chains, and as long as five suspended atoms, with quite large interatomic distances between them [3,6,7]. Here we use realistic molecular dynamics (MD) simulations to understand the formation mechanisms of these atomically thin Au nanowires. We study in detail the evolution of a Au nanowire under stress, and show how defects induce the formation of necks that eventually will form the one-atom chains. After the nanowire's rupture, we analyze the structure of the Au tip, which we believe will be universally present due to its highly symmetric nature.

Gold nanowires have been produced from self-supported strained thin films in high vacuum, under a transmission electron microscope [3,7]. In these experiments, holes are produced in the film using a high intensity irradiation (current density of 100 A/cm^2). Once thin nanometric bridges are formed, they are imaged with a low-intensity electron beam (current density of 30 A/cm^2). The generated metal nanowires, which are under tensile stress, show a tendency to elongate, become thin, in some cases as thin as a single line of atoms, and finally break [7]. These real time image experiments are fundamental to the understanding of the dynamical evolution of structural, electronic, and transport properties in these thin wire structures under stress conditions. However, intrinsic experimental limitations do not allow them to probe in detail the microscopic mechanisms responsible for the evolution of these structures, all the way until their breaking. In order to throw some light on this problem, we have performed an MD simulation, which can help the understanding of these processes at an atomistic level.

Thin wires have been investigated before through the use of MD simulations with classical effective potentials [9,10]. This type of simulation has also made predictions such as the possibility of helical structures as the wires become very thin [8]. However, to describe the dynamical formation of atomically thin wires, including their rupture, it seems to us that the explicit inclusion of electrons in the calculation is an essential feature. Some *ab initio* molecular dynamics simulations have been performed before, however only for simpler systems such as Na nanowires [11,12]. In these simulations there was no indication of the formation of atomically thin chains that are longer than one atom. Moreover, for Au, studies of the breaking using first principles simulations also did not obtain chains that are longer than one atom. Instead, small idealized contacts were first produced, and then studied with first principle techniques [13,14]. To our knowledge, the only simulations that generate atomically thin chains longer than one atom do not include the electrons explicitly, i.e., are all based on some type of effective potential. For Au, a recent study employed first principles, electronic structure calculations for the equilibrium final structures [15]. This study, however, did not consider the dynamics of the formation and breaking of these wires under tensile stress, which is the central issue of the present contribution.

Therefore, we have performed tight-binding molecular dynamics (TB-MD) simulations [16–18]. This method lies in between first principles and empirical methods: it is more accurate than empirical potential methods because it explicitly includes the electronic structure, and is much faster than first principles methods. This TB-MD has been successfully used before [19] to study crystalline and liquid Au. The MD procedure uses the Naval Research Laboratory tight-binding (NRL-TB) parametrization [16,17] for the electronic states [20]. The electronic structure is calculated using a diagonalization procedure. The equations of motion are integrated using the Verlet algorithm and the

time step used was $\Delta t = 1$ fs. To perform the annealing, we have used a friction parameter $\gamma = 0.001$ fs^{-1}. Brillouin zone sampling was done using the Γ point. The periodic supercells used in all calculations had dimensions (20 Å, 20 Å, L_W).

To simulate the dynamical evolution of the wire under stress, we used the following protocol: (i) our simulations start from a stack of ten planes of seven atoms, oriented along the (111) growth direction. The initial periodic supercell has $L_W = 24.0$ Å along the tube direction, which corresponds to an elongation of 0.4 Å (or ~2%) when compared to an ideal stack of ten (111) planes in bulk Au. In order to obtain a more stable relaxed structure, this initial configuration is warmed to 600 K, and then annealed to lower temperatures, which results in a cylindrical final geometry with the surface atoms reconstructing into a densely packed structure; (ii) the wire is elongated by 0.5 Å; (iii) the temperature is increased to 400 K; (iv) the system is annealed for 4000 MD steps (4 ps) up to a temperature of approximately 30 K. Steps (ii)–(iv) are repeated until we observe the rupture of the wire. Even though this protocol corresponds to elongation rates much higher than the experimental ones (but similar to all other rates used in atomistic simulations), it leads to forces that are quite similar to the measured values [14], being between 1.0 and 2.5 nN throughout the simulation. Moreover, we obtain a value for the applied force right before the breaking of the nanowire around 1.8 nN, in very good agreement with the experimental value [14] of 1.5 ± 0.3 nN. Finally, it is worth mentioning that all the general features discussed below were also present in other simulations where we varied either the cell elongation [step (ii) above] or the simulation temperature [step (iii) above].

In Fig. 1 we present six snapshots (Figs. 1a through 1f) of final configurations, obtained following the above protocol, for wire elongations (L_W) between 25.5 and 41.0 Å. As the wire is pulled, the cylinder tends to become hollow, with the central atoms of the seven-atom planes moving out to the surface. In this way, the seven-atom planes are transformed into six-atom rings, which are stacked along the tube axis, as can be seen in Fig. 1a ($L_W = 25.5$ Å). In this configuration, the Au atoms form a tube which is essentially a folded (111)-sheet, similar to what happens in Carbon nanotubes [21]. This is consistent with the fact that the Au atoms always try to expose a closed-packed surface [22]. We observe that a new ring of six atoms is inserted when the increase in the length of the wire is of the order of the (111) interplanar distance in bulk Au (~2.3 Å). When the rings are somewhat compressed, we observe a small helicity along the tube axis. This probably happens in order to accommodate the atoms, and the helicity decreases as the wire is pulled.

In Fig. 1b we see the development of a one-atom neck, which happens when $L_W = 33$ Å. We observe in the interval from $L_W = 31$ Å to $L_W = 34$ Å a force buildup

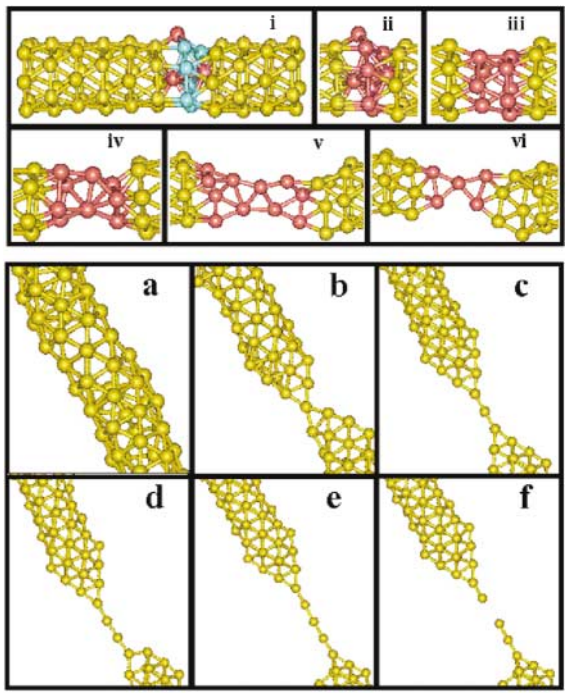

FIG. 1 (color). Atomic configurations of a gold nanowire at selected elongation stages, obtained through tight-binding molecular dynamics simulations. The configurations presented correspond to the following wire lengths: (a) 25.5 Å; (b) 33.0 Å; (c) 37.0 Å; (d) 38.0 Å; (e) 40.5 Å; (f) 41.0 Å. In the upper panel the dynamical evolution of the one-atom constriction is detailed. It shows the defect structure responsible for the neck formation, and its evolution, from $L_W = 27.0$ Å to $L_W = 33.0$ Å. The configuration in (i) shows the defect structure: two interstitial and one external Au atoms (red) surrounding a six Au-atom ring (blue). The evolution of this defect structure [red in (ii)] is depicted from frame (iii) to frame (vi). This final frame corresponds to the one-atom neck displayed in (b).

from 1.2 up to 2.6 nN, right before the formation of the one-atom neck, followed by a sudden force reduction to a value of 1.3 nN. This sawtooth behavior is similar to experimental results [14]. In general terms, the thinning down process is due to a defect structure that leads to the one-atom constriction shown in Fig. 1b. The process is accomplished by surface atoms drifting to the tips as thermodynamics would indicate, as pointed out by Torres *et al.* [13]. Once the one-atom constriction that separates the two tips is formed, a new process is initiated. Atoms from only one of the tips start to move to the neck, and are incorporated to the one dimensional chain that grows as long as five atoms from apex to apex, with three suspended atoms. The details of the neck formation are presented in the upper panel of Fig. 1. We observe that a defect structure, shown in Fig. 1i, is responsible for the development of the neck. This defect structure is composed of two interstitial atoms (red) near a six-atom ring (blue), plus an external atom (red). These defect atoms (red, Fig. 1ii) rearrange themselves into a four-atom ring plus a five-atom ring (red, Fig. 1iii). The five-atom ring, being more unstable

than the four-atom one, further changes into a two-atom and a three-atom structure (Fig. 1iv). A structure similar to a two dimensional ladder develops (Fig. 1v), finally forming the one-atom neck of Fig. 1b, which is also shown in detail at Fig. 1vi. From this point on, the neck starts to grow, incorporating more atoms into the one-atom thick necklace, as can be seen from Figs. 1c to 1e. The dynamical evolution of this one-atom chain shows, similarly to the experiments [7], an apex lateral movement. Finally, when $L_W = 41.0$ Å (Fig. 1f), there is a sudden increase of one of the bond distances from a value of ~3.1 Å to a value close to 4.3 Å, indicating the breaking of the nanowire. Further pull of the wire simply increases this distance. It is worth mentioning that when the necklace breaks, the atomic structure of the unstable tip is similar to the other one. Therefore, it can be said that the wire will break only after the tips attain a rather stable structure. Before this configuration is reached, the system prefers to move the atoms from the less stable positions in the tip towards the neck, rather than breaking the wire. This behavior is similar to what has been recently reported by Rubio-Bollinger *et al.* [14].

The gold nanowire, just before breaking, displays a one-atom thick, five-atom long necklace. A detailed view of this structure is shown in Fig. 2, where all relevant bond distances are displayed. This structure displays longer bonds for the suspended atoms (3.07 and 2.93 Å), whereas the atoms attached to the apexes have shorter bonds. The suspended atoms in fact have their bond lengths oscillating roughly between 2.9 and 3.1 Å. As can be seen, the longest distance that is obtained before the nanowire's breaking is approximately 3.1 Å, with all the other distances along the necklace being between 2.7 and 2.9 Å. Rodrigues and Ugarte [7] obtain, right before the breaking of the nanowire, chains that are 3–4 atoms long (this is also obtained by Ohnishi *et al.* [3]), with interatomic distances between 2.4 and 3.6 Å, with the shorter distances closer to the apex. Our Fig. 2 should be compared with Figs. 1 and 2 from Rodrigues and Ugarte [7], where they show that the one-atom thick necklace is attached to two atoms at the tip. Moreover, a property of our simulation, which is also present in the experimental results of Ref. [7], is the movement of the apex as the nanowire is pulled. Therefore, the general features of our simulation are in quite good agreement with experimental results [7].

When the one-atom neck is formed, we note that one of the tips (the one with four atoms marked in red in Fig. 2) is quite stable. For example, we observe that all the atoms that are incorporated into the one-atom thick necklace are originated from only one side, with the other side acquiring a configuration that does not change upon further pulling. We show this configuration in detail in Fig. 3a. It is composed, from the tube outwards, of layers of 6 (almost a regular hexagon), 6 (distorted hexagon), 4, and 2 atoms (Fig. 3b). Whereas the first six-atom ring is close to a regular hexagon, similarly to the other rings that constitute the cylindrical Au nanotube, the other six-atom ring distorts in order to accommodate the next four-atom layer. As can be seen, the tip resembles a child's French hat (Fig. 3c), being formed basically by two hexagonal structures that share four atoms (red, Fig. 3c) among themselves. This

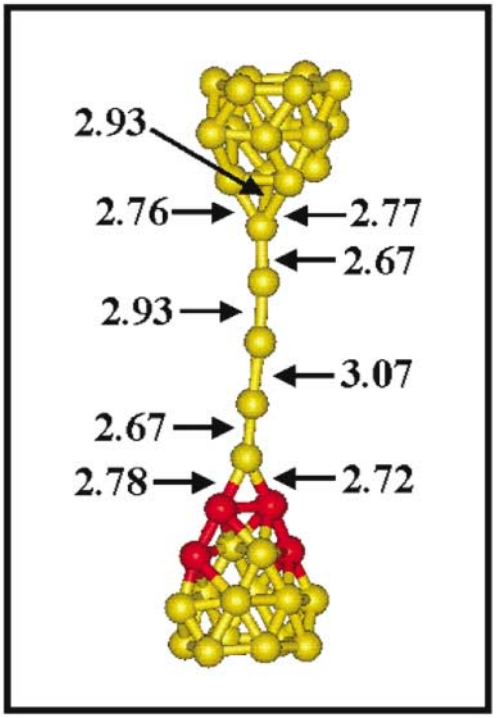

FIG. 2 (color). Structure of the nanowire just before breaking, showing the detail of the one-atom thick necklace. All the bond distances are in Å.

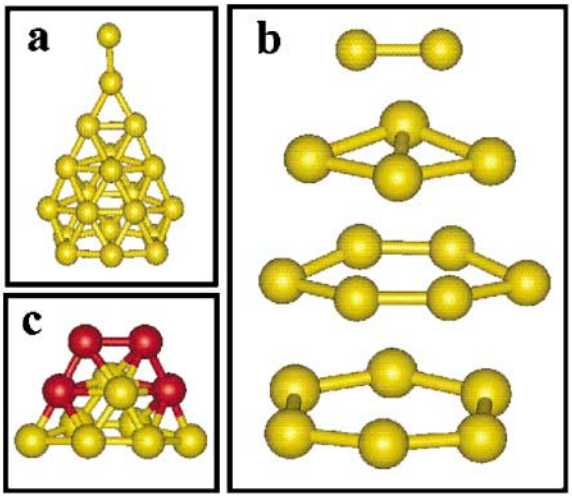

FIG. 3 (color). Stability of the nanowires tip. The tip, before and after the breaking, shows a highly symmetric and stable structure. In (a) the whole tip is shown, whereas in (b) the layers forming it are presented. Finally, in (c) the French hat structure is shown.

structure seems to be quite universal, since different simulations evolved to tips that had basically this structure. Sometimes we observed that instead of a 2,4,6,6, structure, we obtained a 2,3,6,6 configuration, where the two hexagons forming the French hat now shared five atoms. Given the tendency of gold to form closed-packed structures, we believe that the tip structure shown here will be quite ubiquitous, irrespective of the fact that it is going to continue in a tube, as shown here, or if it would continue into a thicker, more bulklike structure, as obtained in some experiments. Further evidence of this probable universality is the similarity between parts of our tip structure and the configurations of Au clusters obtained by Häkkinen and Landman [23].

In conclusion, we have presented a realistic simulation, where the electronic structure is treated explicitly, for the dynamical evolution and the breaking of a Au nanowire. All the main features that we observed in our computer experiments are very similar to the experimental realizations produced in Au films by the beam-hole technique [7]. We show how defects lead to the formation of a constriction in the tube, which evolves into a one-atom thick, five-atom long necklace. Finally, we present a structure for a gold tip which is most likely to be universal, due to its highly symmetric structure. The relevance of the present study rests on the fact that, as the technology progresses towards ever smaller devices, it is fundamental to understand the properties of a gold nanowire and its tip, since they will most likely be used as nanocontacts (to view an animation of this simulation, see [24]).

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[24] See AIP Document No. EPAPS: E-PRLTAO-87-022150 for animation showing evolution of the nanowire/the simulation. This document may be retrieved via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.