Formation of Gold Nanowires with Impurities: A First-Principles Molecular Dynamics Simulation

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(Received 22 December 2006; published 27 February 2007)

We present first-principles molecular dynamics simulations of the formation of monatomic gold nanowires with different impurities (H, C, O, S). Special care was taken not to bias the probability that the impurity atoms participate in the monatomic wire, which is the main focus of this work. Hydrogen always evaporated before the formation of the monatomic chains. Carbon and oxygen were found in the final chains with low probability (~10%), while sulfur almost always participated in it (probabability ~90%). The mean distances between gold atoms bridged by carbon, oxygen, and sulfur were 3.3, 4.4, and 5.0 Å, respectively, in good agreement with experimental observations. The contributions of carbon, oxygen, and sulfur to the density of electronic states at the Fermi level are neglegible, moderate, and large, respectively.

DOI: 10.1103/PhysRevLett.98.096102 PACS numbers: 68.65.−k, 68.37.Lp, 71.15.Mb, 71.15.Pd

Metallic monatomic nanowires have attracted much attention in recent years [1–25] both because they present new physical phenomena and because of their possible applications in nanotechnology. Gold, in particular, has been found to form specially long and stable monatomic chains, observed by high resolution transmission electron microscopy (HRTEM) [4,10,14]. These observations have repeatedly found distances of up to 5 Å between the gold atoms of the chains, much longer than in bulk gold (2.9 Å) or in the gold dimer (2.5 Å). This suggests that there may be unobserved light-atom impurities that act as bridges in the bonds between the gold atoms. These impurities would affect dramatically the mechanical and electronic properties of the chain, and several experimental and theoretical studies have been performed to study their effects. The theoretical simulations typically consider an ideal chain [6,19], sometimes connected to electrode tips [11,15,16,18], with an impurity atom placed by hand at some plausible position. To study their structure and stability, molecular dynamics (MD) simulations and/or geometry relaxations have been also performed, using classical potentials [9] or tight-binding forces [12,20]. Apart from the limited accuracy and reliability of these methods, the main drawback of this procedure is that the presence of the impurity is simply assumed, and no description is obtained of how, when, or with what probability it migrates to its assumed position.

To overcome these limitations, we have simulated, using *ab initio* MD, the formation and growth of gold chains with a variety of impurities, without any assumption on their initial positions. The forces are calculated using density functional theory (DFT), as implemented in the SIESTA method [26,27], with the generalized gradient approximation (GGA) for exchange and correlation [28]. To accelerate the MD we use a combination of cheap and expensive forces [29]. The cheap forces are evaluated every one-femtosecond time step. They are obtained from the non–self-consistent Harris-Foulkes functional [30,31] and an optimized [32] but minimal basis set. The MD trajectories are corrected periodically (every 10 fs) with the expensive forces, calculated with the self-consistent Kohn-Sham functional [33] and an optimized [32] basis set made of double-ζ plus polarization atomic orbitals. We verified that, within the range 1–10 fs, the results did not depend on the period of the force corrections.

To avoid uncertainties on the initial structure [8] and impurity position, we start from an amorphous geometry, obtained by quenching from the liquid a thick vertical column of 50–150 gold atoms in a $40 \times 40 \times (10–20)$ Å simulation cell. We looked for finite size effects and we found that, in this range of values, the resulting monatomic chains did not depend on the number of atoms nor the initial cell size. One or two impurity atoms were introduced, at random substitutional positions, in the middle of the liquid simulation, of ~6 ns at ~2000 K. The amorphous solid columns are stretched during 4–18 ns until they break, generally after forming a monatomic chain of several atoms. The stretching took place every 100–300 fs, by homogeneously rescaling the z atomic coordinates and simulation cell by 1%–3%. To facilitate the flow of atoms, and the evolution of the structure towards stable configurations, during the necessarily short times of the simulations, a relatively high temperature was maintained, by rescaling the velocities every 50 fs. This was also necessary to avoid the heating of the system produced by the work of stretching it. Temperatures between 50 and 1000 K were tried, but most simulations were performed at ~600 K, which was found to be optimal for the formation of long chains. It is important to emphasize that, since we use periodic boundary conditions, there is no bias to where the monatomic chain will form, and no atoms are privileged to participate in it. In principle, the impurity can also

diffuse to or away from the chain, once this is formed, although no such diffusion was observed in practice.

Pure gold simulations were performed first, since we are not aware of previous simulations of the whole formation of the chain, at this level of theory. They produced monatomic chains of up to 8 gold atoms connected to roughly pyramidal tips. Figure 1 is a histogram of the final number of atoms present in the monatomic chain. It agrees well with the experimental values [1]. Although somewhat masked by the high simulation temperature, the wires have the zigzag structure reported previously [6]. Prior to rupture the average angle of the zigzag is 168° and the distance between chain atoms is 2.8 ± 0.2 Å. This distance agrees well with the most frequent experimental value [34]. The mean applied force when the chain breaks depends on the DFT functional used and on the stretching speed. The GGA result (1.8 ± 0.3 nN) for slow stretching (1% every 200 fs) agrees well with the experimental value (1.5 nN) [11] and with previous theoretical calculations [12,17]. For the local density approximation (LDA) we obtain a larger value (2.4 ± 0.2 nN), also in agreement with previous calculations [12]. Faster stretching also leads to larger breaking forces.

Next we simulated the formation of wires with impurities at different temperatures and stretching speeds. Figure 2 shows snapshots of one of these simulations, in which it can be seen how five atoms, including the sulfur impurity, are successively extracted from both tips. The complete movie can be found in [35].

Figure 4 shows, for each species, the fraction of simulations that ended with the impurity in the monatomic chain. Hydrogen always evaporated from the amorphous gold column in less than 300 fs, long before the chain formation. Although this may be obviously related to our high simulation temperature, there is also experimental evidence [36] that HRTEM electrons will knock off any hydrogen impurity. Carbon ended in one simulation as one of the extreme atoms of the chain or, more properly, as one of the vertex atoms of the tip, bonded to the gold chain and to two tip atoms. Snapshots of the simulation can be found in Fig. 3 and the complete movie is in [37]. In all other cases, carbon remained within the bulk or the surface of the tips, with an approximately tetrahedral coordination to three or four gold atoms. In another simulation, an oxygen impurity formed part of the chain itself. Sulphur was the only impurity found consistently to be in the monatomic chain in most of the simulations. In one of these simulations, the chain ended with no less than 15 atoms. When two sulfur impurities were introduced in an aggregate of 98 gold atoms, two different chains formed. In none out of three such simulations we observed two sulfur atoms within a single chain. Of course, this does not imply that

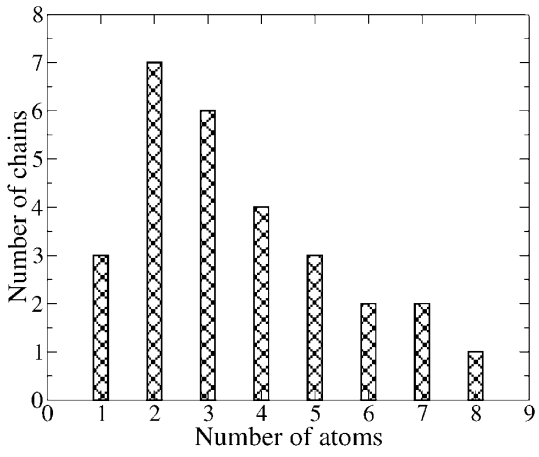

FIG. 1. Histogram of the number of simulations with a given number of atoms in the monatomic chain, just before breaking. The average chain length is 3.6 atoms. There were no impurities present.

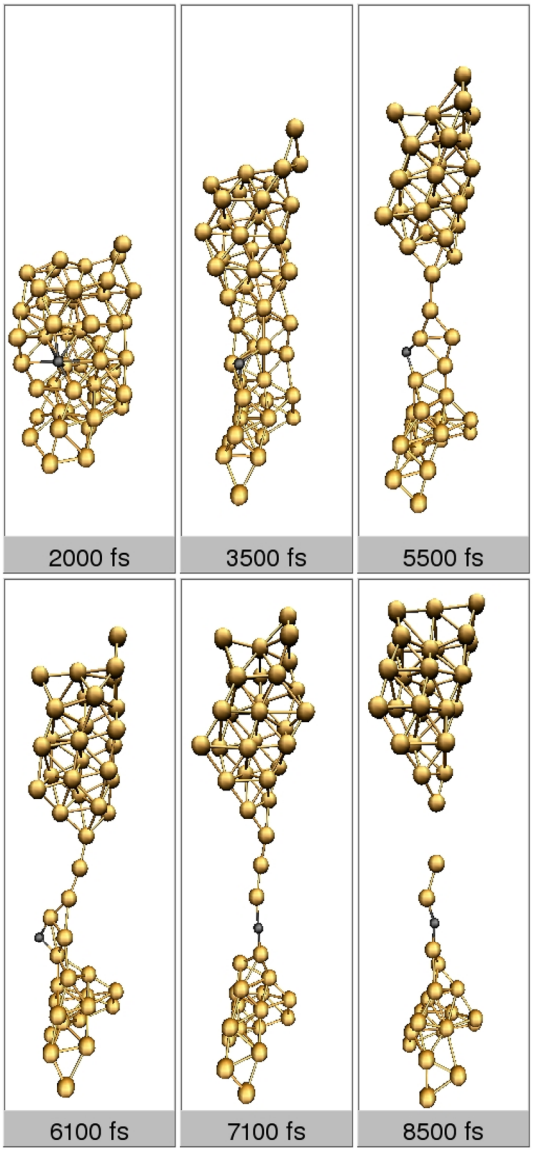

FIG. 2 (color online). Snapshots of the simulation of the formation and growth of a monatomic gold chain with a sulfur atom impurity (represented by a small black sphere). The complete movie can be found in [35].

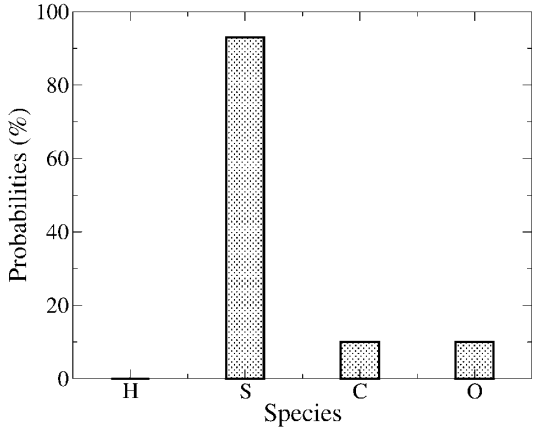

FIG. 3. Probability that impurities of various species participate in the monatomic chains before they break. Hydrogen did not participate in any of the 15 simulations performed with it. Carbon and oxygen ended in the chain in one of ten simulations each. Sulphur was in the chain in 12 out of 13 simulations.

monatomic chains with several impurities cannot occur in the much slower stretchings of real wires. But it indicates that sulfur atoms strongly facilitate the local formation of monatomic chains.

As previously mentioned, the simulation setup used was specifically designed to avoid any bias on the initial neck structure and impurity position. However, we also performed a simulation aimed at describing a plausible process of incorporation of a carbon impurity. In this simulation, a carbon atom landed from the vacuum on a gold wire with a two-shell helical structure [13], at 300 K. The C impurity initially made bonds with three surface gold atoms but, in ~3 ps, it suddenly dived inside the wire and adopted an sp^3 tetrahedrally coordinated position. In this process, it produced some local amorphization of the wire. Upon wire stretching, the carbon impurity ended at the apex of one of the tips, but still tetrahedrally coordinated.

The average distances between gold atoms bridged by carbon, oxygen, and sulfur were 3.3 ± 0.2, 4.4 ± 0.1, and 5.0 ± 0.2 Å, respectively. These values allow one to explain all the experimental distances observed directly by HRTEM [14,21] or indirectly in wire length histograms [25]. They are also in reasonably good agreement with previous static calculations for the same impurities [19,24]. Except for a Au-O bond in a single simulation the chains always break between two gold atoms, so that all the impurities (C, O, S) have a strong bond with gold. It should be also mentioned that the breaking force was unusually large (3.4 nN) in the chain with the carbon impurity, whose simulation was performed with the GGA functional and a slow stretching speed. Since we had a single such case, we cannot conclude whether this result is systematic or anecdotal, however.

Figure 5 shows the Mulliken projected density of electronic states (PDOS) of the C, O, and S impurities within

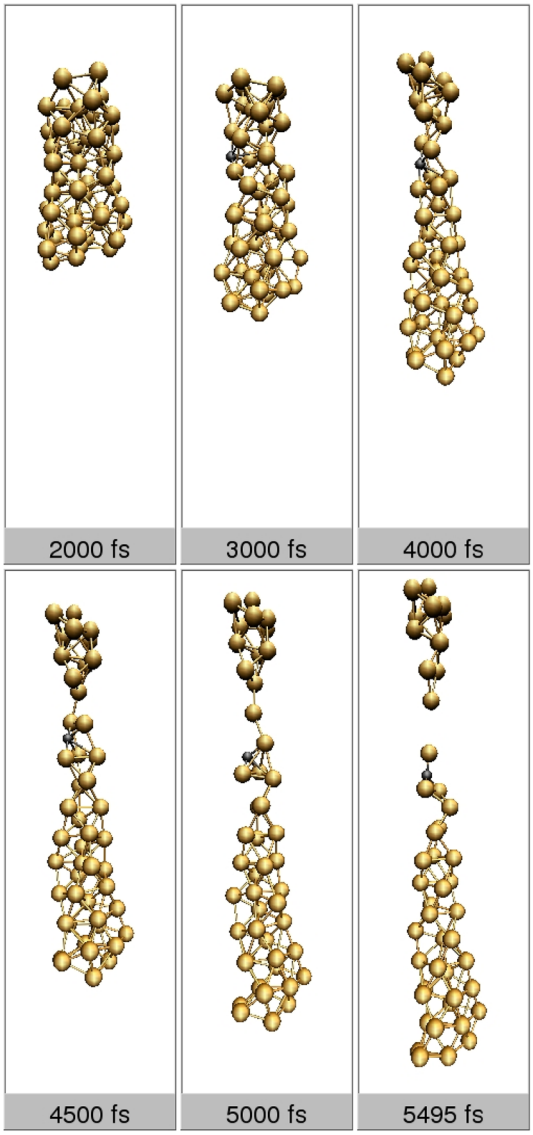

FIG. 4 (color online). Snapshots of the simulation of the formation of a gold wire with a carbon atom impurity (represented by a small black sphere). The carbon atom acts as a tip of one of the pyramids. The complete movie can be found in [37].

the chains, as well as that of a typical gold chain atom. It can be seen that oxygen and specially sulfur have a large contribution to the states at the Fermi level, suggesting that they will not perturb significantly the conductance of the gold monatomic chains. On the contrary, carbon has a negligible PDOS at the Fermi level, suggesting that it may interrupt the conductance. Further studies, of the actual conductance of these chains with impurities, are in progress.

In conclusion, we have simulated the formation of monatomic gold chains in the presence of different impurities (H, C, O, and S). We find that, among them, sulfur is by far the most likely impurity to end up in the chain, although carbon and oxygen have also a finite probability. All the unusually long distances between gold atoms,

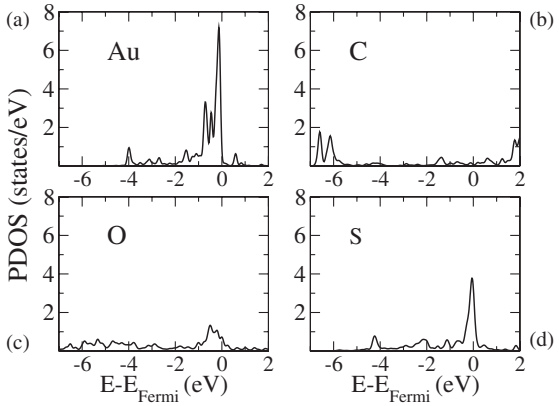

FIG. 5. (a) Projected density of electronic states (PDOS) of a typical atom in a monatomic chain of pure gold. (b)–(d) PDOS of carbon, oxygen, and sulfur impurities in a monatomic chain.

observed experimentally [14,21,25], are reproduced in our simulations for gold atoms bridged by different impurities.

We would like to acknowledge fruitful discussions with N. Agrait, C. Arroyo, J. Riquelme, N. Lorente, G. Román, and Ó. Paz. This work was supported by Spain's MEC Grants Nos. BFM2003-03372 and FIS2006-12117.

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[37] The EPAPS document cited in Ref. [35] contains a movie showing the formation of a gold chain. There is one carbon impurity present that participates as a tip of one of the pyramids. The total simulation time is 5.5 ps.