Stability of gold nanowires at large Au-Au separations

N.V. Skorodumova\textsuperscript{1} and S.I. Simak\textsuperscript{2}

\textsuperscript{1} Department of Materials Chemistry, Uppsala University, Box 538, S-75121, Uppsala, Sweden
\textsuperscript{2} Department of Applied Physics, Chalmers University of Technology and Gothenburg University, S-41296, Gothenburg, Sweden

Abstract

The unusual structural stability of gold nanowires at large separations of gold atoms is explained from first-principles quantum mechanical calculations. We show that undetected light atoms, in particular hydrogen, stabilize the experimentally observed structures, which would be unstable in pure gold wires. The enhanced cohesion is due to the partial charge transfer from gold to the light atoms. This finding should resolve a long-standing controversy between theoretical predictions and experimental observations.
Gold is known as the noblest metal of all due to its inert behavior as a bulk material and low reactivity of its perfect surfaces. This property made gold probably the most valuable and desirable metal in modern human history. At the same time, it still challenges scientists with some puzzling features. Among them there are striking structural and electrical properties of gold nanocontacts. Such nanocontacts are obtained by the mechanically controllable break-junction (MCB) technique or by the scanning tunneling microscopy (STM), when the tip is first driven into the gold sample, and then retracted forming a nanowire [1–3]. On stretching the nanowire undergoes a number of structural rearrangements finally producing a monoatomic gold bridge suspended between the tip and sample. In most experiments such nanowires are found to be amazingly stable, reaching the interatomic distances of about 3.6 - 4.0 Å i.e. significantly larger than the nearest-neighbor distance in bulk gold (2.88 Å). The conductance of the nanocontacts is quantized in steps of $2e^2/h$ approaching the theoretical one-dimensional limit of $2e^2/h$ when the suspended wire becomes monoatomic [2,3].

A different approach to produce and study gold nanowires is based on the transmission electron microscopy (TEM). In this technique gold nanowires are fabricated by perforating holes in a gold thin film using a focused electron beam with current density $\sim 100$ A/cm$^2$. The structural reorganization of the nanowire is further studied by the electron beam with current density either reduced to $\sim 30$ A/cm$^2$ or kept the same as in the preparation process [2,4]. The results of the former experiments generally agree with the results of the STM and MCB based experiments, finding long gold interatomic distances of 3.4 - 3.6 Å [4]. On the contrary, the latter experiment does not confirm the existence of long Au-Au bonds, reporting the bulk-like spacing of $\sim 2.9$ Å.

The issue of the novel gold nanowires has already been addressed in a large body of theoretical and experimental works which describe many important features of gold nanocontacts, including their formation, structural rearrangements and conducting properties. However, a convincing explanation of the puzzling structural stability of gold monoatomic wires at large Au-Au separations, seen in most experiments, is still lacking. In the present report we show from first-principles quantum mechanical calculations that the unusual structural stability of gold nanowires at large separations of gold atoms can be explained by the presence of undetected light atoms able to stabilize the experimentally observed structures, which would be unstable in pure gold wires. In particular, we find hydrogen to be a primary suspect.

To understand the origin of the phenomena we have performed first-principles calculations in the framework of the density functional theory (DFT) [13]. Two sets of data have been calculated at $T = 0$ K, first, for the gold nanowires supported by gold tips consisted of 28 atoms, with monoatomic part consisted of 2 to 6 atoms, and second, for infinite monoatomic chains with the similar number of gold atoms treated as inequivalent in the periodically reproduced unit cells. In agreement with previous findings [7,10], the results obtained for both sets (with and without supporting tips) are very similar, indicating that the stability of a nanocontact is essentially determined by its monoatomic part. No magnetization is found for any studied configuration. The binding energy curve for an infinite gold monoatomic wire is given in Fig. 1(a) together with the equilibrium atomic configurations and the ranges of their stability. Zigzag is an energetically favorable atomic configuration. Upon stretching the wire becomes linear at the Au-Au distance of about
2.7 Å remaining stable only in a narrow interval up to about 2.9 Å, when the Peierls distortion triggers the dimerization of the wire accompanied by a metal-insulator transition (Fig. 1(a)). Decreasing the Au-Au distance below the range shown in Fig. 1(a) leads to a series of deepening local energy minima and corresponds to the chain folding into the bulk-like structure.

These results suggest the wire to break (and obviously stop being conductive) already at interatomic distances of 2.9 Å, in agreement with previous calculations [7–10] and the experiment by Takai et al. [5]. They, however, by no means explain the stability of gold monoatomic wires with the spacing of 3.4 - 4.0 Å observed in most of other experiments [2–4]. Therefore the existing first-principles theory does not provide a complete description of the phenomenon. It is especially remarkable regarding the fact that very different gold systems (bulk, surface, dimers, atomic clusters), and in particular their geometry, are known to be accurately described in the framework of the DFT [14]. It seems to be a reasonable question to ask if there could be anything missing in the previous theoretical considerations of gold nanowires. For instance, it is tempting to check whether small amounts of light atoms, which are hard to detect in standard experiments, may influence the stability of gold nanocontacts.

We start with an observation that very similar results for the Au-Au spacing (3.4 - 4.0 Å) have been obtained in different experiments, with and without (ultra) high vacuum conditions, in situ sample preparation, and controlled low temperature [2–4,15]. Especially in the case of the ultra-high vacuum the probability to encounter most of the light atoms, such as, for instance, carbon and oxygen, is expected to be low. In particular it has been shown by Ugarte [16] and Rodrigues and Ugarte [4] that in the TEM-based experiments intense electron irradiation is helpful against carbon contamination. Nevertheless, such experiments [4] still show large Au-Au distances in gold nanowires. There is, however, at least one element, hydrogen, which is present even at high vacuum conditions [17,18]. It is also known that gold becomes recognizably active when deposited as small particles on a substrate [19–21]. This enhancement of gold reactivity is caused by a high concentration of steps and surface defects in small particles, as well as by the substrate-induced strain [22]. Note that such low-dimensional gold structures are well presented on the surfaces of the STM tips. Gold surfaces interact with atomic hydrogen, which is able to form a stable layer on the surface [23]. Dissolving into the bulk, hydrogen tends to segregate at the surface and subsurface layers [24]. Gold has also been reported to play a role of a hydrogen trap in gold alloys that may be considered as an indication of a strong interaction between gold and hydrogen atoms [25].

We have extensively studied this interaction from first-principles in the systems of different scales: from nanostructures to the fcc bulk gold [26]. Our results show that hydrogen molecules do dissociate when embedded into the gold matrix. Moreover, being dissolved in small quantities in the fcc bulk gold, hydrogen binds strongly to Au atoms with characteristic Au-H distances of about 1.75 Å. Moderate stress and deformations of the gold host lattice do not break these bonds making hydrogen follow Au atoms.

The most profound influence of the hydrogen presence has been observed in gold nanowires. The binding energy curve for a one-dimensional gold-hydrogen wire is presented in Fig. 1(b). There is a sequence of structural transformations similar to that of a pure gold wire (see Fig. 1(a)). A zigzag arrangement of atoms is most stable for Au-Au
distances smaller than 2.7 Å, followed upon stretching by the linear configuration of the gold atoms with zigzag-like positions of the hydrogen atoms. This configuration is stable up to about 3.4 Å of Au-Au distance. On further stretching the chain becomes linear with hydrogen placed in between the gold atoms reaching the Au-Au spacing of about 3.8 Å and Au - H spacing of 1.85 Å. Further stretching results in dimerization eventually followed by the complete break of the wire. Thus monoatomic gold-hydrogen wire shows an enhanced stability at large Au-Au distances that well matches the experimentally observed spacing of 3.6 - 4.0 Å [2–4]. The cohesion is twice as strong as the one of a pure gold chain (see Fig. 1). As experiments on gold nanowires are often performed at room temperature, we have also studied the stability of monoatomic Au-H wires at finite temperatures by first-principles molecular dynamics (MD) simulations [27]. According to our MD simulations the structures of the nanowires obtained at T = 0 K remain intact at least up to T = 300 K.

The nature of bonding in gold nanocontacts containing hydrogen can be understood by analyzing the charge density as well as the difference between the actual charge density and the atomic densities of gold and hydrogen constituting the system (Fig. 2). Charge density presented in Fig. 2(a) reveals pronounced electron density bridges caused by hydrogen situated in between the gold atoms. This resembles the hydrogen-type bonding where the charge transfer from Au to H, which can be seen in the charge density difference plot (Fig. 2(b)), is a key component. Therefore, an enhanced effective binding between the gold atoms via Au-to-H charge transfer mechanism results in the striking stability of the gold-hydrogen nanowires.

Further, in experiments [2–4] the conductance of gold nanocontacts has been measured at a low d.c. bias (about 10 mV). We have also studied the stability and ability of the gold-hydrogen chains to conduct at a similar bias, which is simulated by shifting the chemical potential at one end of the wire with respect to the other in the way described in Ref. [28]. The band structure of such a wire (Fig. 3) clearly shows the existence of one conduction channel, in agreement with theory and most experimental findings [2–4]. Additional forces appearing on atoms due to the applied bias are of about 0.001 eV/Å that is by no means sufficient for breaking the bonds.

In general one cannot rule out the possibility of the presence of other light elements. First, small amount of light atoms can be already present in the sample used to fabricate a nanowire. Second, not all experiments on gold nanowires employ high vacuum conditions. We have considered carbon and oxygen as possible contaminants (see Ref. [13] for calculational details) and found that both of them stabilize monoatomic wires up to the Au-Au distances of ∼ 4.5 Å. The enhanced cohesion is due to the bonding mechanism similar to the one operating in Au-H wires. The equilibrium Au-Au distances in Au-O and Au-C wires are, however, somewhat larger (∼ 3.6 Å in both systems). Thus we notice that due to the larger equilibrium Au-Au separation in such systems, they should be in a "compressed" state in the region of experimentally observed Au-Au distances, contrary to the Au - H system. Therefore, if in a particular experiment oxygen or carbon atoms are responsible for the increased stability of gold nanowires, one would at least expect a different dependence of the force on the tips displacement from what is actually seen in the STM-based experiments [10].

Further, we comment on the experimental results by Takai et al. [5] reporting the
bulk-like spacing in gold monoatomic wires and, therefore, confirming the theoretical results for pure gold wires. We suggest that this experiment was most probably free of contamination due to a permanent use of intense electron irradiation (current density $\sim 100 \text{ A/cm}^2$) during the observations. As a result, gold nanowires were stable at a bulk-like atomic separation of 2.9 Å within a very short time interval. It is in a sharp contrast with other experiments [2,4], where an electron beam with current density of 100 A/cm$^2$ was only used to perforate neighboring holes in gold films while the observations were performed at essentially lower current density ($\sim 30 \text{ A/cm}^2$). As we already mentioned, these experiments resulted in long-living monoatomic wires with large interatomic distances.

To summarize, we have shown that the striking stability of the suspended gold nanowires may be attributed to the hydrogen atoms, which mediate gold-gold interactions, dramatically increasing binding. Hydrogen, being always present but rarely controlled in experiments, alters the properties of gold nanowires, the crucial components of nanometer-scale devices developed for microelectronics and biophysics applications [29]. In addition we note that other light atoms, like carbon and oxygen, are also able to stabilize gold nanowires. Our calculations show that Au-O and Au-C monoatomic wires are stable up to the Au-Au distances of 4.5 Å. We suggest that further experiments, incorporating hydrogen and other light atoms detection, may lead to important implications for the modern atomic-size technologies.

We thank M. Springborg, K. Hermannson, Y. Andersson, K. Forsgren, G. Källén, S. Kubatkin and D. Erts for discussions. Support from the Swedish Foundation for Strategic Research and Swedish Research Council is gratefully acknowledged.
REFERENCES

[1] Y. Kondo, K. Takayanagi, Science 289, 606 (2000).
[2] H. Ohnishi, Y. Kondo, K. Takayanagi, Nature 395, 780 (1998).
[3] A. I. Yanson, G. R. Bollinger, H. E. van den Brom, N. Agraït, J. M. van Ruitenbeek, Nature 395, 783 (1998).
[4] V. Rodrigues and D. Ugarte, Phys. Rev. B 63, 073405 (2001).
[5] Y. Takai, T. Kawasaki, Y. Kimura, T. Ikuta, and R. Shimizu, Phys. Rev. Lett. 87, 106105-1 (2001).
[6] U. Landman, W. D. Luedtke, B. E. Salisbury, and R. L. Whetten, Phys. Rev. Lett. 77, 1362 (1996).
[7] D. Sánchez-Portal et al., Phys. Rev. Lett. 83, 3884 (1999).
[8] L. De Maria, M. Springborg, Chem. Phys. Lett. 323, 293 (2000).
[9] N. V. Skorodumova and S. I. Simak, Comp. Mat. Sci. 17, 178 (2000).
[10] G. Rubio-Bollinger, S. R. Bahn, N. Agraït, K. W. Jacobsen, S. Vieira, Phys. Rev. Lett. 87, 026101-1 (2001).
[11] V. Rodrigues, T. Fuhrer, D. Ugarte, Phys. Rev. Lett. 85, 4124 (2000);
[12] Y. Kondo, H. Kimata, H. Ohnishi, K. Takayanagi, J. Electron Microsc. 48, 1081 (1999).
[13] Calculations were done by all-electron projector augmented-wave (PAW) method [30,31] based on the DFT within the generalized gradient approximation (GGA) [32]. The cut-off of 312 eV for Au and Au - H systems, and 500 eV for Au - C and Au - O were used. One-dimensional chains were simulated by the three dimensional periodic tetragonal supercells with chains along z-axis and separated in x and y directions by 14 Å. Hellmann-Feynmann forces were systematically calculated, and the nuclei steadily relaxed to equilibrium positions. The integration over the Brillouin zone was performed on a 1x1x24 k-point mesh. According to the convergence tests, this was a relevant amount for an accurate description (within 1 meV per atom) of the energy differences in question.
[14] In particular, with the method used here (see Ref. [13]) the lattice parameter of the bulk gold is reproduced within 1 % accuracy. An example of DFT calculation of gold surfaces can be found in Ref. [34]. Discussion of the properties of gold clusters of different size calculated within DFT can be, for instance, found in Refs. [1,33,34]
[15] H. Ohnishi, Y. Kondo, K. Takayanagi, Surf. Sci. 415, L1061 (1998).
[16] D. Ugarte, Nature 359, 707 (1992); D. Ugarte, Chem. Phys. Lett. 209, 99 (1993).
[17] E. Abramov, D. Eliezer, Hydrogen Effects in Materials. Edited by A. W. Thompson and N. R. Moody, 295 (1996).
[18] J. F. O’Hanlon, A User’s Guide to Vacuum Technology. John Wiley & Sons, New York, 387-396 (1989).
[19] M. Valden, X. Lai, D. W. Goodman, Science 281, 1647 (1998).
[20] G. C. Bond, Catal. Rev.-Sci. Eng. 41(3&4), 319 (1999).
[21] A. Sanchez et al., J. Phys. Chem. 103, 9573 (1999).
[22] M. Mavrikakis, P. Stoltze and J. K. Nørskov, Catal. Lett. 64, 101 (2000).
[23] I. Čadež, R. I. Hall, M. Landau, F. Pichou, C. Schermann, J. Chem. Phys. 106, 4745 (1997).
[24] L. Stobiński and R. Duš, Appl. Surf. Sci. 62, 77 (1992).
The first-principles molecular dynamics (MD) simulations, as implemented in Ref. 30 were performed in the canonical ensemble using the Nosé thermostat 33 for temperature control. The forces acting on the atoms were calculated from the ground-state electronic energies according to the Hellmann-Feynman theorem at each time step and subsequently used in the integration of Newton’s equation of motion. The temperature of 300 K was used throughout the MD simulations.

T. N. Todorov, J. Hoekstra, and A. P. Sutton, Phil. Mag. B 80, 421 (2000).

J. K. N. Mbindyo et al., Adv. Mat. 13, 249 (2001).

G. Kresse and J. Furthmüller, Comp. Mater. Sci. 6, 15 (1996); G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996); G. Kresse and J. Joubert, Phys. Rev. B 59, 1758 (1999).

P.E. Blöchl, Phys. Rev. B 50, 17953 (1994).

J. P. Perdew et al. Phys. Rev. B 46, 6671 (1992).

S. J. Nosé, Chem. Phys. 81, 511 (1984).

B. Hammer and J.K. Nørskov, Nature 376, 238 (1995).

H. Häkkinen and U. Landman, Phys. Rev. B 62, R2287 (2000).

O. D. Häberlen, S. Chung, M. Stener, N. Rösch, J. Chem. Phys 106, 5189 (1997).
FIGURES

FIG. 1. Binding energy curves for infinite monoatomic wires of pure gold (a) and gold with hydrogen (b). The shown energies are given per gold atom (a) and gold-hydrogen pair (b) as a function of the average Au-Au distances. These are calculated as \((d_1 + ... + d_n)/n\), with \(d_n\) being the actual distances between gold atoms in linear chains or the z-projected distances for zigzag-like chains [9], where \(n\) is the number of gold atoms per unit cell. For infinite monoatomic wires the total amount of hydrogen atoms (case (b)) is equal to the total amount of gold atoms resulting in 2 to 6 hydrogen atoms per simulated nanowire (see Fig. 2). The energy curves for the chains forced to be strictly linear (with all \(d_n\) equal) are shown in blue. The equilibrium atomic configurations are given in the corresponding ranges of their stability. The underlined intervals indicate the range of stability of the chains with the linear arrangements of gold atoms.

FIG. 2. Charge density distribution (a) and the difference between the actual density and atomic charge densities of gold and hydrogen constituting the system (b) for the monoatomic part of the gold-hydrogen nanocontact with the Au-Au distance of 3.6 \(\text{Å}\). Charge density in (a) spans the range 0 - 1 electron/\(\text{Å}^3\) with the spacing of 0.1 electron/\(\text{Å}^3\). Charge density difference in (b) spans the range -0.1 - 0.2 electron/\(\text{Å}^3\) with the spacing of 0.03 electron/\(\text{Å}^3\). In both (a) and (b), the color background changing from blue via green and red to yellow indicates the increase of the density. Accordingly, in the charge density difference plot (b) the blue part of the spectrum indicates the lack and the red and yellow ones the excess of electrons. Positions of Au and H nuclei are marked with corresponding symbols.

FIG. 3. The band structure of the gold-hydrogen nanowire with the Au-Au distance of 3.6 \(\text{Å}\) (see Fig. 1) calculated on a sufficiently dense mesh of k-points (30 k-points in both, \(\Gamma Z\) and \(\Gamma X\) directions). The energy is given with respect to the Fermi level. The perfectly flat bands in \(\Gamma X\) direction indicate the absence of interaction between single nanowires simulated in three-dimensional periodic supercells.
