Effect of Impurities in the Breaking of Gold Nanowires

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ABSTRACT

Using *ab initio* Density Functional Theory total energy calculations, we study the influence of H, B, C, N, O, and S in the rupture of a gold nanowire. In particular, using an as realistic as possible model for a suspended gold nanowire under stress, we observe that the Au wire always break at an Au-Au bond, with a maximum bond length between 3.0 and 3.1 Å. Therefore, the experimentally observed large Au-Au bonds before the rupture of the nanowire (≈ 3.6 Å) is probably due to the presence of light impurities (X) forming Au-X-Au bonds. We obtain that the Au-Au maximum distance for X equals C or N is of the order of 3.9 Å, whereas for B and O it is of the order of 4.1 Å. On the other hand, H this maximum distance before the rupture of the wire is approximately 3.6 Å, being the best candidate to explain the experimental results. An experimentally observed very large Au-Au bond of 4.8 Å is probably caused by an Au-S-Au structure, since we obtain for this configuration an Au-Au distance of ≈ 4.7 Å.

Keywords: Metallic nanowires. Gold. Computer simulations.

1 INTRODUCTION

Metallic nanowires, and in particular Au nanowires, have been the focus of many recent studies, the main motivations coming from their potential role in nanoelectronics as well as from a fundamental attempt to understand the behavior of matter as the size of the system approaches the atomic limit. Surprisingly large and stable Au-Au interatomic distances, in the range of 3.6-4.0 Å, have been reported by various experimental groups [1-3] in suspended gold nanowires right before their ruptures. From a theoretical viewpoint, no one has been able to reproduce the above mentioned large distances for clean nanowires, the maximum obtained values being of the order of 3.0-3.1 Å, results that are in agreement with recent experimental observations [4]. In an attempt to explain these results we have decided, therefore, to systematically study the effect of impurities in gold nanowires under stress. Few previous works [3,5,6] have tried to explain the Au-Au large distances through impurities, however, some of their assumptions were somewhat unrealistic. In view of this fact, we have decided to reanalyze, using an as realistic as possible model, the influence of C, H, B, N, O and S in the breaking of Au nanowires.

2 COMPUTATIONAL METHODS

To investigate the effect of impurities on the rupture of Au nanowires, we have used a procedure that (i) is based in a quite realistic structure for the nanowire, specially around the impurity atom; (ii) considers the wire to break under stress conditions; (iii) does not have impurities in all bonds, which allows the system to break either at an Au-Au bond, as in a clean wire, or at an Au-X-Au bond, where X is any one of the impurities we study (the whole procedure is explained in detail elsewhere [7]).

The wire we have used in all our calculations is a 70 Au atoms that we have recently obtained through a tight-binding molecular dynamics (TBMD) simulation [8]. Just before breaking it displays an one-atom thick, five-atoms long necklace, attached to quite stable tips structure (see Figure 1). This configuration was used as a starting point for all our calculations with impurities, which were placed in between two Au atoms. However, we now use first-principles total energy Density Functional Theory (DFT) [9] calculations with numerical orbitals as basis sets (we use a split-valence double-zeta basis set with polarization function). We have used the SIESTA code [10], which performs fully self-consistent calculations solving the Kohn-Sham (KS) equations. For the exchange-correlation potential we used a generalized gradient approximation [11]. The ions-valence electrons attraction is described via standard norm conserving pseudopotential [12]. We use periodic-boundary conditions and a supercell approximation with lateral separation of 20 Å between wires to make sure that they do not interact with each other, and we have used the Γ point for the Brillouin zone sampling. We then pulled the wire quasi-statically, always allowing the whole system to relax between pulls until all the force components were smaller than 0.03 eV/Å. This procedure was repeated until the rupture of the wire.

3 RESULTS AND DISCUSSION

Before we considered any impurity in the system, we pulled the clean wire until it broke. The maximum Au-Au distance obtained in this case was approximately 3.1 Å. This result is similar to what we have obtained before in our TBMD simulation [8], and is in good agreement with both the results of Takai *et al.* [4] and the position of the first peak in a histogram of experimentally observed maximum Au-Au distances [3]. Moreover, when we include the impurities, we find that the system always

breaks at an Au-Au bond with maximum bond length between 3.0 and 3.1 Å, as can be seen in Table 1. Similar findings have been obtained in simulations of molecules pulled out of a gold surface [13]. All these results strongly indicate that in nanowires under tension the limit for the pure Au-Au breaking distance is around 3.1 Å, which leads to impurities as the explanation for the large Au-Au distances.

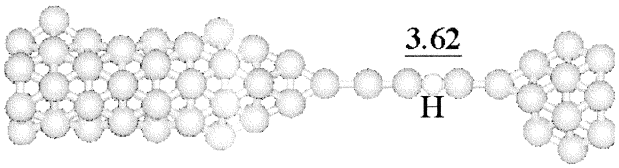

Figure 1: Atomic configuration of a gold nanowire with H atom as an impurity, right before the breaking point. The Au-Au distance of 3.62 Å is in excellent agreement with the reported distances of 3.6 ± 0.2 Å [3].

We present in Table 1 the maximum Au-Au distances for the Au-X-Au structure in the wire, *i.e.,* the distance between Au atoms with an impurity X between them. As can be seen, C and N give a value for this distance of 3.9 Å, whereas B and O give 4.1 Å. On the other hand, H atoms give for the Au-X-Au distance a value of 3.6 Å (see Figure 1), a result that is in excellent agreement with the experimental results [3], suggesting that H impurities are most likely the source of the yet unexplained large Au-Au distances in the range of 3.6 ± 0.2 Å.

X	Au-X-Au (Å)	$(Au-Au)_B$ (Å)	Force (nN)
C	3.9	3.1	1.5
H	3.6	3.1	1.7
B	4.1	3.1	1.9
O	4.1	3.0	1.7
N	3.9	3.0	2.0
CC	5.3	3.1	1.8
S	4.7	3.1	1.7

Table 1: The effect of impurities X in the interatomic distances between Au atoms in the suspended gold neck (see Figure 1), for the chains just prior to breaking. The Au-X-Au is the distance between two Au atoms with an X impurity inserted between them, the $(Au-Au)_B$ represents the size of the Au-Au bond that breaks, and the maximum pulling forces are presented in the last column.

An extremely large Au-Au distance (≈ 4.8 Å) has also been observed experimentally [3], and it has been previously suggested [3] that this distance could be caused by two C atoms inserted into the Au nanowires. However, from Table 1 it can be seen that we obtain that these C-C impurities under stress would result in excessively large distances (≈ 5.3 Å), and we propose that S atoms could be the explanation for this experimental observation, since they give an Au-X-Au distance of 4.7 Å, a value in very good agreement with the experimental result.

Finally, we also report in Table 1 the critical forces before the wire's rupture. As can be seen, they are all in the range of 1.5-2.0 nN, which nicely agree with the experimental findings of Rubio-Bollinger *et al.* [14].

4 CONCLUSIONS

In conclusion, we have shown that neither TBMD [8] nor *ab initio* simulations of the rupture of pure nanowires can explain the experimentally observed Au-Au distances in the range of 3.6 Å, and therefore they are most likely the effect of light impurities. To this end we investigated a series of impurities (C, H, N, O, B, and S) and we conclude that the Au-Au distance of 3.6 Å might be due to the presence of H. Moreover, the much longer event of 4.8 Å [3] might be explained by contamination with S. We hope that our results will stimulate experimentalist to investigate, in a controllable way, the presence of contaminants in the formation, evolution and breaking of Au chains.

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REFERENCES

[1] H. Ohnishi, Y. Kondo and K. Takayanagi, Nature 395, 780; 1998.

[2] V. Rodrigues, T. Fuhrer and D. Ugarte, Phys. Rev. Lett. 85, 4124; 2000; V. Rodrigues and D. Ugarte, Phys. Rev. B 63, 073405; 2001.

[3] S. B. Legoas, D. S. Galvão, V. Rodrigues and D. Ugarte, Phys. Rev. Lett. 88, 076105, 2002.

[4] Y. Takai *et al*, Phys. Rev. Lett. 87, 106105; 2001.

[5] S. R. Bahn *et al.*, Phys. Rev. B 66, 081405; 2002.

[6] N. V. Skorodumova and S. I. Simak, cond-mat/0203162; 2002.

[7] F. D. Novaes, A. J. R. da Silva, E. Z. da Silva and A. Fazzio, Phys. Rev. Lett. accepted for publication.

[8] E. Z. da Silva, A. J. R. da Silva and A. Fazzio, Phys. Rev. Lett. 87, 256102; 2001.

[9] P. Hohenberg and W. Kohn, Phys. Rev. 136, 864B; 1964; W. Kohn and L. J. Sham, Phys. Rev. 140, 1133A; 1965.

[10] P. Ordejón, E. Artacho and J. M. Soler, Phys. Rev. B 53, 10441; 1996; D. Sáanchez-Portal, P. Ordejón, E. Artacho and J. M. Soler, Int. J. Quantum Chem. 65, 453; 1997; E. Artacho, D. Sánchez-Portal, P. Ordejón, A. García and J. M. Soler, Phys. Stat. Sol. (b) 215, 809; 1999, and references therein.

[11] J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett. 77, 3865; 1996.

[12] N. Troullier and J. L. Martins, Phys. Rev. B 43, 1993; 1991.

[13] D. Krüger *et al.*, Phys. Rev. Lett. 89, 186402; 2002.

[14] G. Rubio-Bollinger *et al.*, Phys. Rev. Lett 87, 26101; 2001.