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The Role of Carbon Contamination in Metallic Nanowires

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Metallic nanowires have attracted much attention in the last years due to new phenomena such as quantum conductance and the existence of unexpected long interatomic distances attaining 0.3-0.5 nm. These large distances represented a challenge for physical interpretation. In this work we present experimental data from high-resolution transmission electron microscopy and results from *ab initio* calculations for suspended gold chains and show that these large distances can be easily explained by the presence of carbon atoms as contaminants. In principle the present conclusions can be also applied to other metallic nanowires (such as Ag and Pt) whose structures also present large interatomic distances.

Keywords: *gold nanowires, quantum conductance, carbon contamination*

1. Introduction

A considerable effort has been devoted in the last years to understand the formation mechanisms and conductance properties of metallic contacts and suspended chains at nanoscale[1-7]. Experimental techniques such as scanning tunneling microscopy[1,8-10], high-resolution transmission electron microscopy (HRTEM)[4,5,11-15], and mechanically controllable break junction[14,16,17] have made possible to make such nanosized objects.

Recently, Ohnishi *et al*.[4], using HRTEM set up to the study of gold nanowires (NWs), have revealed the existence of suspended linear atom chains (ATCs), whose conductance was measured to be quanta of conductance, $G_0 = 2e^2/h$ (where e is the electron charge and h is the Planck's constant). Long interatomic distances (ranging 0.35-0.40 nm) were observed which contrast with the usual nearest-neighbor distance in gold bulk (0.28 nm), or in Au_2 dimer (0.25 nm). Other experimental studies also reported anomalously long distances, frequently varying in the 0.29-0.36 nm range[3-5,14,18], however extremely long distances close to 0.5 nm[19] were rarely observed.

Most of the reported long distances in metal ATCs are based on gold. However, they have been also observed in silver and platinum nanowires[20-22], indicating that some common feature might be responsible for these unexpected results. Many theoretical studies have been carried out using different techniques[6,23-25], such as molecular dynamics and density functional formalism trying to explain these unusual distances but large interatomic distances in the range of 0.5 nm have not been obtained from the simulations. However, preliminary calculations[26] considering the possibility of the presence of structural contamination produced an excellent agreement with the experimental data. More recently, first-principles geometrical optimization studies of gold atomic chains[27,28] added new data in support to the presence of contaminants.

In this work we report both experimental and theoretical studies on the formation of suspended gold linear nanowires, addressing the calculations to analyze the origin of the anomalously long distances experimentally observed. Based on experimental information, the idea of nanoatomic chains being contaminated by some impurities[15] during sample fabrication was explored. Due to experimental conditions on the HRTEM[6,14] set up the most probable impurity candidates are carbon atoms. Besides that the presence of carbon atoms would be undetectable in HRTEM images owing to its low contrast[15], producing the illusion of large unusual gold-gold distances.

2. Methodology

In the experimental step, gold nanowires were gener-

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ated *in situ* in a HRTEM (JEM 3010 URP, 300 kV, 0.17 nm resolution, at LME/LNLS Campinas, Brazil) using the method developed by Takayanagi's group[4,13]. The microscope electron beam (current density 100 A/cm^2) is focused on a self-supported polycrystalline gold thin film (5 nm thick, deposited on a holey carbon grid) to drill holes at different sites until nanometric bridges are formed between neighboring holes. To perform the atomic resolution image acquisition the electron beam intensity is reduced up to ~ 30 A/cm^2. A digital camera (Gatan MSC794, acquisition time 1 s) was used to acquire micrographs and a high sensitivity TV camera (Gatan 622SC, 30 frames/s) was used to register NW real-time evolution. This procedure allows us to generate stables NW (life time 1-10 min).

The calculations were performed using *ab initio* density functional total energy methods. We used DMOL[29] and TITAN[30] packages. A double numerical basis set with polarization functions was considered for DMOL and the LACVP**[31] basis set for TITAN. The exchange-correlation part of the total energy is treated in the local density approximation with a Wang-Perdew[32] (Vosko-Wilk-Nusair)[33] parametrization for the DMOL (TITAN) case. We used molecular clusters in order to investigate the origin of the long interatomic distances observed in gold NWs. The structures were generated in a way that the gold atoms are at arbitrary positions forming linear chains with interatomic distances of ~ 0.40 nm. The carbon atoms were positioned at ~ 0.15 nm above the middle chain positions. Fully geometrical optimizations were then carried out. No hydrogen or dummy termination atoms were used[30,31]. Recent first principles density functional studies on suspended gold chains[5] showed that the geometries for naked finite and infinite structures are essentially the same. We have also investigated other atoms (N, O, S, and Si) as possible contaminants. However, results for C contamination produced the best agreement with experimental data.

3. Results and Discussions

In Fig. 1 we show a sequence of snapshots of the gold nanowire formation. The electron beam creates holes in the gold film. These holes increase in size in time and nanometric bridges are formed between neighboring ones [Fig. 1a]. The NWs are generated between apexes of different crystallographic orientations that are in continuous slow relative movement. Even so, the generated NWs display an enhanced stability (lifetime ~ minutes) because NW, apexes and surrounding region form a monolithic system. In some cases the apexes slide, as indicated by an arrow in Fig. 1b. Although the NWs are stables, they elongate spontaneously and become thinner [show by an arrow in Fig. 1c]. Before the NW rupture linear chains (ATC) can be formed whose length is in the 2-4 atoms range [Figs. 1d and 1e]; these

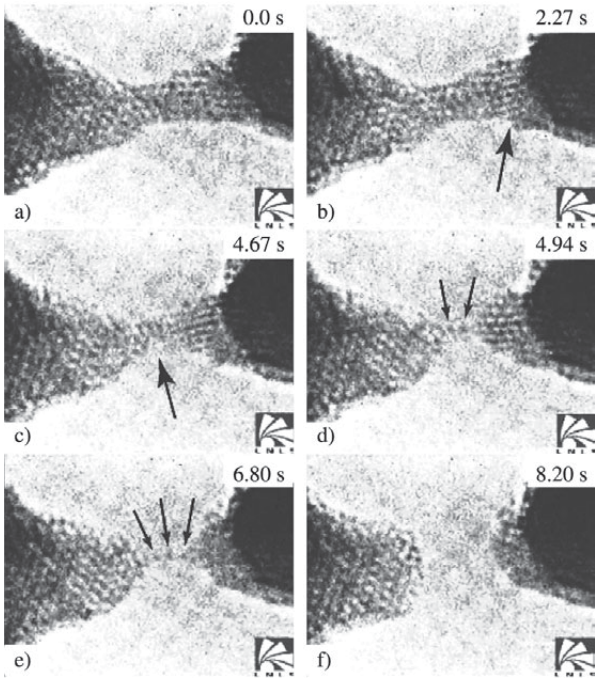

Figure 1. Gold nanowire time evolution. An ATC with two atoms is formed in (d), and in (e) the number of atoms have increased to three in the linear chain (indicated by arrows). See text for discussions.

linear chains may last several seconds. Perhaps, the most surprising fact on ATCs is the interatomic bond length values which are 0.29 - 0.36 nm, or even as long as 0.50 nm[19].

In order to understand the origin of the unexpected large gold-gold interatomic distances, we simulate different ATC geometries. In Fig. 2 we present our results for some selected structures obtained with DMOL. TITAN optimizations produced similar results. When one carbon atom is included between two neighboring gold atoms, the resulting Au-Au distance is in the order of 0.36 nm. When no impurity atom is considered, the interatomic distances are in the 0.24–0.25 nm range. Experimentally, the most frequent distances observed range from 0.29 to 0.36 nm, which suggest that these values are the result of a combination of clean and contaminated linear chains.

In the case of C_2 incorporation, our results show a separation of ~ 0.5 nm between neighboring gold atoms. Many theoretical works were unable to reproduce these long interatomic distances, because they did not consider the possibility of carbon contamination. The presence of carbon atoms in HRTEM experiments are highly probable due to the many possible sources of contamination, such as vacuum oil from rotatory and diffusion pumps, grease and rubber O-rings, etc.. Besides that, recent experimental and

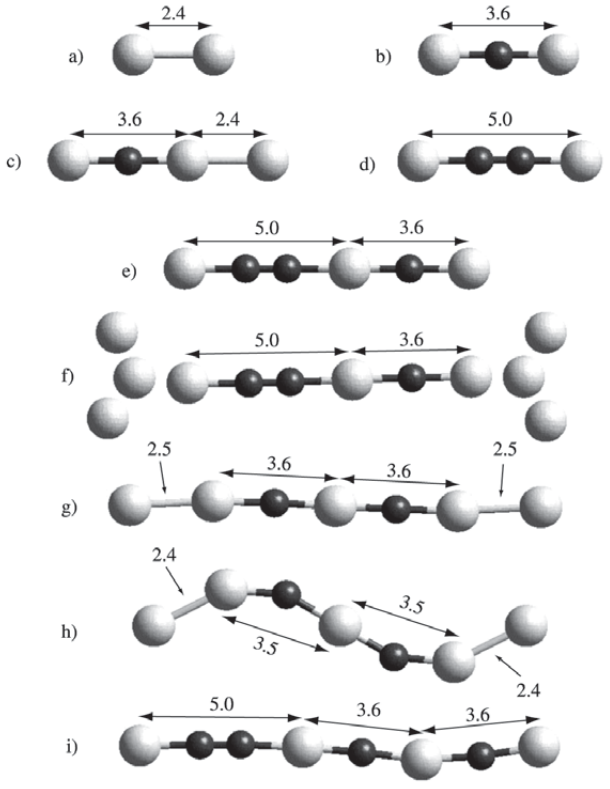

Figure 2. Optimized gold structures with carbon impurities, for selected configurations. In (a) is shown a gold dimer, with bond length in agreement with experimental data. The other chains incorporate carbon impurities. In the different cases the optimized Au-Au distances are compatible with experimental values. The system in (f) is a gold-carbon chain with suspended tips at the ends. We can observe in (c), (g), and (h) situations where the presence of carbon impurity does not affect the bond length of carbon-free Au-Au. Only the structure in (h) had its ends fixed, while all the other were free to relax.

theoretical investigations[21] on the relationship between the formation of Au nanowires and their transport behavior, seem to support the hypothesis that carbon contamination is the main responsible for the anomalously long interatomic distances observed in linear atom chains. In the work of Rego *et al*.[21] they measured the conductance of gold ATCs, and observed a considerable decreasing of conductance plateaus after a few hours. Following an Extended-Hückel approach, Rego *et al*. calculated the conductance in linear chains with carbon atoms included in it, and their results were in good agreement with the experimental observation.

4. Conclusions

We have experimentally analyzed the formation of stable linear gold atom chains, having obtained direct real-space information on atomic positions and bond lengths. We observed anomalously long interatomic distances. To explain the origin of these large gold-gold distances, we have performed *ab initio* geometrical optimization calculations in a local density framework for some gold clusters assuming the presence of carbon atoms as impurity contamination. Our results show that the unexpected long interatomic Au-Au distances (0.4 – 0.5 nm) observed can be easily explained considering the presence of C_2 impurities between the gold atoms forming the linear chain. Bond length values below 0.36 nm might be explained considering a mixture of clean stressed bonds and those contaminated by single carbon atoms. Our results are supported by recent experimental and theoretical investigations on the conductance of gold nanowires. These conclusions can be applied in principle to other metallic nanowires.

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References

1. Landman, U.; Luedtke, W.D.; Burnham, N.A.; Colton, R.J. *Science*, v. 248, p. 454, 1990.
2. Landman, U.; Luedtke W.D.; Salisbury, B.E.; Whetten, R.L. *Phys. Rev. Lett.*, v. 77, p. 1362, 1996.
3. Yanson, A.I.; Rubio Bollinger, G.; van den Brom, H.E.; Agraït, N.; van Ruitenbeek, J.M.; *Nature (London)*, v. 395, p. 783, 1998.
4. Ohnishi, H.; Kondo, Y.; Takayanagi, K. *Nature (London)*, v. 395, p. 780, 1998.
5. Sánchez-Portal, D.; Artacho, E.; Junquera, J.; Ordejón, P.; García, A.; Soler, J.M. *Phys. Rev. Lett.*, v. 83, p. 3884, 1999.
6. Rodrigues, V., Ugarte, D., *Phys. Rev. B*, v. 63, p. 073405, 2001.
7. Kizuka, T.; Umehaa, S.; Fujisawa, S. *Jpn. J. Appl. Phys.*, v. 240, p. L71, 2001.
8. Olesen, L.; Lægsgaard, E.; Stensgaard, I.; Besenbacher, F.; Schiøtz, J.; Stoltze, P.; Jacobsen, K.W.; Nørskov, J.K. *Phys. Rev. Lett.*, v. 72, p. 2251–2254, 1994.
9. Agraït, N.; Rodrigo, J.G.; Vieira, S. *Phys. Rev. B*, v. 47, p. 12345, 1993.
10. Pascual, J.I.; Mendez, J.; Gomez-Herrero, J.; Baro, A.M.; García, N.; Thien Binh, Vu, *Phys. Rev. Lett.*, v. 71, p. 1852, 1993.
11. Kizuka, T.; Yamada, K.; Deguchi, S.; Naruse, M.; Tanaka, N. *Phys. Rev. B*, v. 55, p. R7398, 1997.
12. Kizuka, T. *Phys. Rev. Lett.*, v. 81, p. 4448, 1998.
13. Kondo, Y.; Takayanagi, K. *Phys. Rev. Lett.*, v. 79, p. 455, 1997.

14. Rodrigues, V.; Fuhrer, T.; Ugarte, D. *Phys. Rev. Lett*., v. 85, p. 4124, 2000.
15. Koizumi, H.; Oshima, Y.; Kondo, Y.; Takayanagi, K. *Ultramicroscopy*, v. 88, p. 17, 2001.
16. Muller, C.J.; van Ruitenbeek, J.M.; de Jongh, L.J. *Physica (Amsterdam)*, v. 191C, p. 485, 1992.
17. Krans, J.M.; van Ruitenbeek, J.M.; Fisun, V.V.; Yanson, I.K.; de Jongh, L.J. *Nature (London)*, v. 375, p. 767, 1995.
18. Takai, Y.; Kawasaki, T.; Kimura, Y.; Ikuta, T.; Shimizu, R. *Phys. Rev. Lett*., v. 87, p. 106105, 2001.
19. Kondo, Y.; Takayanagi, K. *Bull. Am. Phys. Soc*., v. 44, p. 312, 1999.
20. Rodrigues, V.; Bettini, J.; Rocha, A.R.; Rego, L.G.C.; Ugarte, D. *Phys. Rev. B*, v. 65, p. 153402, 2002.
21. Rego, L.G.C.; Rocha, A.R.; Rodrigues, V.; Ugarte, D. submitted for publication in Phys. Rev. B.
22. Rodrigues, V.; Ugarte, D. *Phys. Stat. Sol. B*, v. 230, p. 475, 2002.
23. Häkkinen, H.; Barnett, R.N.; Landman, U. *J. Phys. Chem. B*, v. 103, p. 8814, 1999.
24. Sørensen, M.R.; Brandbyge, M.; Jacobsen, K.W. *Phys. Rev. B*, v. 57, p. 3283, 1998.
25. Okamoto, M.; Takayanagi, K. *Phys. Rev. B*, v. 60, p. 7808, 1999.
26. Legoas, S.B.; Galvão, D.S.; Rodrigues, V.; Ugarte, D. *Phys. Rev. Lett.*, v. 88, p. 076105, 2002.
27. Novaes, F.D.; da Silva, A.J.R.; da Silva E.Z.; Fazzio, A. *Phys. Rev. Lett*., v. 90, p. 036101, 2003.
28. Skorodumova, N.V.; Simak, S.I. *Phys. Rev. B*, v. 67, p. 121404, 2003.
29. Delley, B. *J. Chem. Phys.*, v. 92, p. 508, 1990; v. 113, p. 7756, 2000. DMOL3 is available from Accelrys, Inc. as part of Materials Studio and the Cerius2 program suites. http://www.accelrys.com.
30. TITAN is a program suite from Wavefunction, Inc. http://www.wavefun.com.
31. LACVP** represents a basis set (developed at Los Alamos National Laboratory) with effective core potentials (ECP). It includes the outermost core orbitals and contains the highest *s* and *p* (*s*, *p*, and *d*) shells for main group atoms (transition metals).
32. Wang, Y.; Perdew, J.P. *Phys. Rev. B*, v. 43, p. 8911, 1991.
33. Vosko, S.J.; Wilk, L.; Nusair, M. *Can. J. Phys.*, v. 58, p. 1200, 1980.