J|A|C|S
ARTICLES

Published on Web 12/08/2008

Rate-Dependent Energy Release Mechanism of Gold Nanowires under Elongation

Qing Pu,[†] Yongsheng Leng,*[,†,‡] and Peter T. Cummings[†,§]

Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, Tennessee 37235, and Department of Mechanical and Aerospace Engineering, The George Washington University, Washington, D.C. 20052

Received August 9, 2008; E-mail: leng@gwu.edu

Abstract: The mechanism of the formation of different junction structures of gold nanowires under stretching has been studied by comprehensive molecular dynamics (MD) simulations using the second-moment approximation of the tight-binding (TB-SMA) potential. The simulations (540 MD runs in total) reveal that there is an inherent rate-dependent energy release law that unifies the effects of the system size, the temperature, and elongation rate on the dynamic elongations of gold nanowires.

1. Introduction

Understanding the mechanisms of the formation of break-junction structures derived from metal nanowires has important scientific and technological applications in molecular electronic devices.[1−4] The formation of single-atom metallic chains (or monatomic chains) has attracted tremendous interest in both experimental and theoretical studies due to their inherent quantum effects in many physical properties. A simple way to generate an ultrathin nanowire is through the so-called mechanically controllable break-junction technique (MCBJ).[2,5−7] In MCBJ experiments, a notched gold wire is attached to a flexible substrate that will be bent to stretch and break the wire. Single-atom contact in the break junction can be established with the aid of such a fine adjustment system. After the breaking process, the two freshly broken apexes can be brought into contact repeatedly under the precise control of the distance between the two contacts. Many theoretical studies have investigated this experimental procedure at both quantum mechanical and classical molecular simulation levels. These theoretical works studied not only the quantum conductance properties[8−12] but also the mechanical behaviors of nanowires under stretching[8−16] and the break-junction structures.[9,10,12,13,17−20]

Recent development in high-resolution transmission electron microscopy (HRTEM) techniques allows direct observation of the break junction process with atomic resolution and, simultaneously, the measurement of electron transport through the junction.[21,22] However, very long abnormal Au−Au bond lengths in monatomic chains were discovered,[21−23] which was later attributed to the insertion of light foreign atoms, such as oxygen atoms.[24] Monatomic chain formation has been studied by molecular dynamics (MD) simulations[10,13,17] using different classical potentials for transition metals. The stability and breaking forces of these single-atom chains have been further studied by density functional theory (DFT) calculations,[9,12] including our recent work.[25] The HRTEM experiment performed by Kondo and Takayanagi[26] also found the multishell helical structures for very thin gold nanowires (<1.5 nm in diameter),

[†] Vanderbilt University.
[‡] The George Washington University (present address).
[§] Nanomaterials Theory Institute, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831.

(1) Cui, X. D.; Primak, A.; Zarate, X.; Tomfohr, J.; Sankey, O. F.; Moore, A. L.; Moore, T. A.; Gust, D.; Harris, G.; Lindsay, S. M. *Science* **2001**, *294*, 571–574.
(2) Reed, M. A.; Zhou, C.; Muller, C. J.; Burgin, T. P.; Tour, J. M. *Science* **1997**, *278*, 252–254.
(3) Xu, B. Q.; Tao, N. J. J. *Science* **2003**, *301*, 1221–1223.
(4) Nitzan, A.; Ratner, M. A. *Science* **2003**, *300*, 1384–1389.
(5) Krans, J. M.; Vanruitenbeek, J. M.; Fisun, V. V.; Yanson, I. K.; Dejongh, L. J. *Nature* **1995**, *375*, 767–769.
(6) Muller, C. J.; Vanruitenbeek, J. M.; Dejongh, L. J. *Phys. Rev. Lett.* **1992**, *69*, 140–143.
(7) Untiedt, C.; Yanson, A. I.; Grande, R.; Rubio-Bollinger, G.; Agrait, N.; Vieira, S.; van Ruitenbeek, J. M. *Phys. Rev. B* **2002**, *66*, 085418.
(8) Mehrez, H.; Ciraci, S. *Phys. Rev. B* **1997**, *56*, 12632–12642.
(9) Rubio-Bollinger, G.; Bahn, S. R.; Agrait, N.; Jacobsen, K. W.; Vieira, S. *Phys. Rev. Lett.* **2001**, *87*, 026101.
(10) Sorensen, M. R.; Brandbyge, M.; Jacobsen, K. W. *Phys. Rev. B* **1998**, *57*, 3283–3294.
(11) Todorov, T. N.; Sutton, A. P. *Phys. Rev. B* **1996**, *54*, 14234–14237.
(12) Jelinek, P.; Perez, R.; Ortega, J.; Flores, F. *Phys. Rev. B* **2008**, *77*, 115447.
(13) Finbow, G. M.; LyndenBell, R. M.; McDonald, I. R. *Mol. Phys.* **1997**, *92*, 705–714.
(14) Landman, U.; Luedtke, W. D.; Salisbury, B. E.; Whetten, R. L. *Phys. Rev. Lett.* **1996**, *77*, 1362–1365.
(15) Tanimori, S.; Shimamura, S. *J. Phys. Soc. Jpn.* **1999**, *68*, 3556–3561.
(16) Gall, K.; Diao, J. K.; Dunn, M. L. *Nano Lett.* **2004**, *4*, 2431–2436.
(17) Coura, P. Z.; Legoas, S. B.; Moreira, A. S.; Sato, F.; Rodrigues, V.; Dantas, S. O.; Ugarte, D.; Galvao, D. S. *Nano Lett.* **2004**, *4*, 1187–1191.
(18) da Silva, E. Z.; da Silva, A. J. R.; Fazzio, A. *Phys. Rev. Lett.* **2001**, *87*, 256102.
(19) Torres, J. A.; Tosatti, E.; Dal Corso, A.; Ercolessi, F.; Kohanoff, J. J.; Di Tolla, F. D.; Soler, J. M. *Surf. Sci.* **1999**, *426*, L441–L446.
(20) Tosatti, E.; Prestipino, S.; Kostlmeier, S.; Dal Corso, A.; Di Tolla, F. D. *Science* **2001**, *291*, 288–290.
(21) Ohnishi, H.; Kondo, Y.; Takayanagi, K. *Nature* **1998**, *395*, 780–783.
(22) Rodrigues, V.; Fuhrer, T.; Ugarte, D. *Phys. Rev. Lett.* **2000**, *85*, 4124–4127.
(23) Rodrigues, V.; Ugarte, D. *Phys. Rev. B* **2001**, *6307*, 73405.
(24) Thijssen, W. H. A.; Marjenburgh, D.; Bremmer, R. H.; van Ruitenbeek, J. M. *Phys. Rev. Lett.* **2006**, *96*, 26806.
(25) Pu, Q.; Leng, Y. S.; Tsetseris, L.; Park, H. S.; Pantelides, S. T.; Cummings, P. T. *J. Chem. Phys.* **2007**, *126*, 144707.
(26) Kondo, Y.; Takayanagi, K. *Science* **2000**, *289*, 606–608.

 © 2008 American Chemical Society

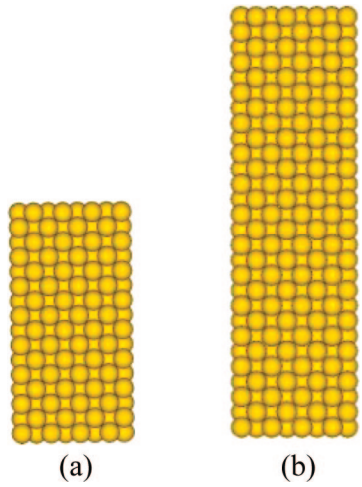

Figure 1. Initial molecular configurations of Au (001) nanowires: (a) Au256 and (b) Au448.

which have been studied by Wang et al.[27] using the glue model potential.[28]

We have recently examined the relative utility of different classical potentials for the energetic description of gold atoms and concluded that for very small gold clusters, particularly for very low coordination systems, the second-moment approximation of the tight-binding (TB-SMA) potential[29] is the most suitable one for describing their energetic and structural properties.[25] In the present paper, we report MD simulations with TB-SMA potential to explore the effects of the system size, the temperature, and stretching rate on the elongation properties of gold nanowires. Extensive MD runs provide us with a detailed picture of the statistical nature of the occurrence of different junction structures before break, yielding fundamental new insights.

2. Simulation Approach

Our previous comparative studies showed that the TB-SMA[29] potential can give a much better energetic description on the structure and dynamic properties of a finite gold nanowires.[25] In the present work, we are interested in a fundamental question related to the condition of the occurrence of Au monatomic chains. Out of many effects upon this monatomic chain formation, we focus on the effects of system size, temperature, and elongation rate of gold nanowires. Thus, comprehensive MD simulation runs will be performed. Here, two different Au nanowires with different lengths along the [001] direction at various temperatures and elongation rates will be investigated. The shorter nanowire includes 16 layers of gold atoms with a total of 256 atoms (Figure 1a). The longer nanowire contains 28 layers of gold atoms with a total of 448 atoms (Figure 1b). The lengths of the shorter and longer nanowires (hereafter, we call them the Au256 and Au448 nanowires) are 30.6 and 55.1 Å, respectively. The two layers at both ends are kept rigid, and the atoms between them are dynamic. Stretching the gold nanowires is performed by displacing the top two rigid layers with increments of 0.1 Å, followed by relaxations of the whole

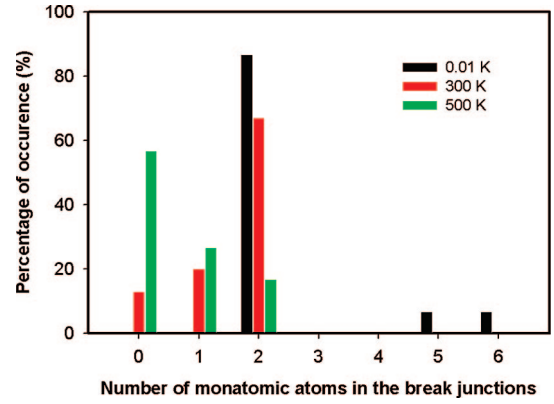

Figure 2. Histogram of the occurrence of monatomic chains in the break junctions for Au256 at the elongation rate of 1.0 m/s.

Table 1. Averaged Total Elongations (in Å) of Au256 and Au448 Right before the Break at Different Temperatures and at an Elongation Rate of 1.0 m/s

	Au256	Au448
0.01 K	18.8 ± 2.1	30.7 ± 12.0
300 K	18.3 ± 4.1	21.3 ± 7.4
500 K	15.8 ± 3.1	12.8 ± 3.2

system for 10, 100, and 200 ps with a time step of 2 fs. These correspond to elongation rates of 1.0, 0.1, and 0.05 m/s. The equations of motion are integrated via the velocity−Verlet algorithm, and the temperatures are controlled at 0.01, 300, and 500 K by the Nosé−Hoover thermostat.[30−32] All of the results shown below are based on statistical studies. In each case, 30 independent MD runs are performed to obtain the averaged total elongations and individual break-junction structures are monitored, resulting in 540 MD runs in total.

3. Results from the Detailed Case Studies

Table 1 summarizes the averaged total elongations right before the break of Au256 and Au448 at temperatures of 0.01, 300, and 500 K for 1.0 m/s elongation rate. It is found that the averaged total elongations vary with temperature for both nanowires, but with different trends. Figures 2 and 3 present the corresponding histograms of the percentage of the occurrence of monatomic chains with different atomic lengths.

For Au256, the difference of the averaged total elongations at 0.01 and 300 K are insignificant. However, the averaged total elongations for Au448 decrease from 30.7 to 21.3 Å as the temperature increases from 0.01 to 300 K. This different elongation behavior for the Au256 and Au448 comes from the very long monatomic chains formed for Au448 at 0.01 K, as shown in the histogram in Figure 3. The counts of long monatomic chains (beyond 2-atom in length) increase from 13% for Au256 to 43% for Au448 at 0.01 K. Specifically, 13-atom monatomic chains are obtained for the Au448 at 0.01 K. At 300 K, only 2-atom monatomic chains are formed for both gold nanowires. The formation of longer monatomic chains for Au448 at 0.01 K appears to be related to the more gold atoms being involved in the elongation. This increase in the number

(27) Wang, B. L.; Yin, S. Y.; Wang, G. H.; Buldum, A.; Zhao, J. J. *Phys. Rev. Lett.* **2001**, *86*, 2046–2049.
(28) Ercolessi, F.; Parrinello, M.; Tosatti, E. *Philos. Mag. A* **1988**, *58*, 213–226.
(29) Cleri, F.; Rosato, V. *Phys. Rev. B* **1993**, *48*, 22–33.
(30) Martyna, G. J.; Tuckerman, M. E.; Tobias, D. J.; Klein, M. L. *Mol. Phys.* **1996**, *87*, 1117–1157.
(31) Nose, S. *J. Chem. Phys.* **1984**, *81*, 511–519.
(32) Tuckerman, M.; Berne, B. J.; Martyna, G. J. *J. Chem. Phys.* **1992**, *97*, 1990–2001.

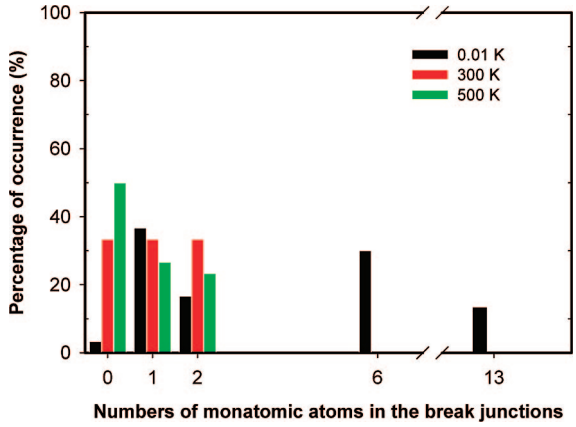

Figure 3. Histogram of the occurrence of monatomic chains in the break junctions for Au448 at the elongation rate of 1.0 m/s.

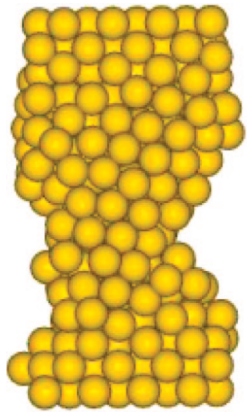

Figure 4. Initial distorted molecular configuration of Au256 at 500 K.

of gold atoms in Au nanowires will generally extend their relaxation times, which will be discussed further in this paper.

When we further increase the temperature to 500 K, the averaged total elongations decrease dramatically for both nanowires (see Table 1). The histograms in Figures 2 and 3 show that the probability of the formation of longer monatomic chains decreases as the temperature increases. At 300 and 500 K, there is no single case of monatomic chains longer than two atoms. Since monatomic chains correspond to high energy states, it is not difficult to understand that at elevated temperatures, the chains will become unstable due to strong thermal fluctuations and diffusion of gold atoms. We even found that at 500 K significant relaxation of Au256 occurred prior to pulling, leading to the formation of a distorted neck (see Figure 4). We have shown that the diffusion of gold atoms at this elevated temperature becomes quite significant.[33] The initial distorted configuration makes the break of gold nanowires much faster. A recent Monte Carlo simulation study[15] also found the similar phenomenon which showed that a 62-atom-Au (001) nanowire broke much earlier at 600 K than at 300 K.

In order to understand how the elongation rate influences the break junction structures, we decrease the elongation rate from 1.0 m/s to 0.1 and 0.05 m/s. Tables 2 and 3 list the averaged total elongations for Au256 and Au448 under these elongation rates at different temperatures. The main findings from these case studies are summarized below.

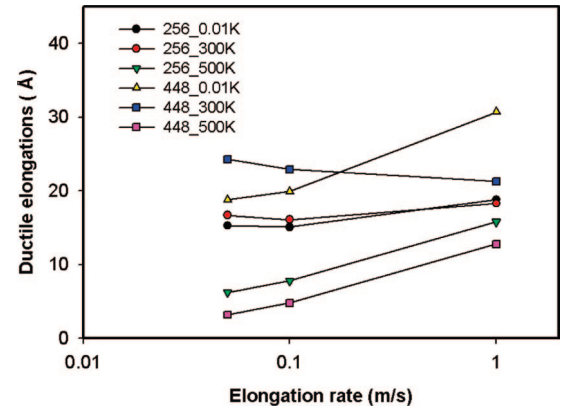

Figure 5. Variations of the averaged total elongations versus elongation rate for Au256 and Au448 at different temperatures.

Table 2. Averaged Total Elongations (in Å) of Au256 Right before the Break at Different Temperatures and at Elongation Rates of 0.1 and 0.05 m/s

	0.1 m/s	0.05 m/s
0.01 K	15.1 ± 0.4	15.3 ± 0.0
300 K	16.1 ± 6.9	16.7 ± 3.5
500 K	7.8 ± 1.2	6.2 ± 0.9

Table 3. Averaged Total Elongations (in Å) of Au448 Right before the Break at Different Temperatures and at Elongation Rates of 0.1 and 0.05 m/s

	0.1 m/s	0.05 m/s
0.01 K	19.9 ± 4.2	18.8 ± 4.7
300 K	22.9 ± 7.4	24.3 ± 9.3
500 K	4.8 ± 1.4	3.2 ± 1.5

Compared with the cases of elongations at 1.0 m/s (Table 1), the averaged elongations at low elongation rates (0.1 and 0.05 m/s) are generally less than those at 1.0 m/s, except for the Au448 at 300 K. We also see slightly increases in elongations at 300 K than at 0.01 K. Under such low elongation rates, we do not obtain monatomic chains longer than two atoms for Au256, and only find one case of 9-atom monatomic chain for Au448 at 0.01 K. The probability of the formation of longer monatomic chains (over two atoms) for Au448 decreases from 43% at 1.0 m/s to 3% at 0.05 m/s (see Figure 3 and the Supporting Information).

Figure 5 summarizes the total elongations of Au256 and Au448 as a function of elongation rate at different temperatures. In most cases, they increase with the elongation rate, mainly because of the longer monatomic chains formed at high stretching rates. The only exception is the Au448 at 300 K, for which very long 3-atom thick helical structures are obtained at the lowest elongation rate. This type of helical structure is the thinnest helical structure compared with those observed in the HRTEM experiment.[26] A recent MD simulation study[34] using the embedded atom method (EAM) potential[35] also found the similar structure. Our detailed MD simulations show that about 27% of MD runs for Au448 eventually end up with the helical chains at 0.05 m/s (see the Supporting Information). We find that this comparably stable structure can be as long as 23 Å. Figure 5 also shows that the total elongations at 500 K are very small compared to the cases at 0.01 and 300 K, since significant

(33) Pu, Q.; Leng, Y. S.; Zhao, X. C.; Cummings, P. T. *Nanotechnology* **2007**, *18*, 424007.

(34) Park, H. S.; Zimmerman, J. A. *Phys. Rev. B* **2005**, *72*, 054106.
(35) Daw, M. S.; Baskes, M. I. *Phys. Rev. B* **1984**, *29*, 6443–6453.

diffusion of gold atoms at this temperature results in a very early junction break.

In all of these studies, we found that most Au−Au bond lengths in monatomic chains vary from 2.48 to 2.6 Å, and occasionally the Au−Au bond lengths can be as large as 2.74−2.90 Å at elevated temperature due to thermal fluctuations. These results are consistent with those obtained by using either classical potential or quantum mechanical calculations[10,36] and are also consistent with recent DFT calculations when a foreign oxygen atom was incorporated into the Au monatomic chains.[12,37] We never found any cases of Au−Au bond lengths exceeding 3.0 Å. These were in contrast to the HRTEM experimental findings[21−23] which were later attributed to the contaminated impurities (light foreign atoms) in gold monatomic chains.[24,38] The Au−Au bond breaking forces have not been further monitored in the present work. However, our previous study using TB-SMA potential for gold yielded a value of 1.5 nN,[25] which was surprisingly consistent with the experimentally observed average value (1.5 ± 0.3 nN) by Rubio-Bolinger et al.[9] This Au−Au bond strength at such a low coordination condition (two for each gold atom in the chain), as discussed by Bahn and Jacobsen,[36] is about three times stronger than the bulk value.

4. Discussion: The Rate-Dependent Energy Release Mechanism

To illuminate the underlying mechanism of the formation of different junction structures under different combined effects, and particularly why the long monatomic chain structure at sufficiently low stretching rate is not favored, we first note that any single atomic chain structure will have a high energy state due to the very low coordination environment. The creation of such a high energy state is one way to release the internal strain energy imposed by external stretching. However, there are many other ways to release the strain energy through the formation of other defects, such as the low energy lattice dislocations if the loading rate is sufficiently slow. This is because there is a wide spectrum of mechanical relaxation processes in the contacts.[11] The way of releasing strain energy by the system depends on how fast its relaxations of certain modes of defects compared to the external loading rate. If the system relaxation of certain type of defect is faster than the external loading rate (in other words, the relaxation time of the formation of such defect is shorter than the characteristic time of loading), then the formation of such defect should be dominant in the elongation process. This "rate-dependent energy release" mechanism can be further understood if we look at what really happens for the gold nanowire under elongation. Figure 6 shows the molecular configurations of 2- and 5-atom monatomic chains of Au256 at 0.01 K. These two shorter and longer monatomic chains are generated at elongation rates of 0.05 and 1.0 m/s, respectively. We should emphasize that at very low elongation rate of 0.05m/s, all the break junction structures of 30 independent MD runs for Au256 end up with the 2-atom chains, and most of the structures are similar to that shown in Figure 6a (see the Supporting Information). The detailed animations demonstrate that almost all the Au256 nanowires yield well-defined dislocations initiated along (111) planes,[10] accompanied by significant (111) reconstructions at the (100) facets [see the compact (111) patches in Figure 6a, where many surface gold atoms have a *surface* coordination number of six, rather than four in (100) facet]. The creation of these low energy defects certainly requires much longer time. For comparison, the junction structure that contains 5-atom monatomic chain in Figure 6b has less compact (111) patches. We find that the difference in total energy between the two junction structures is roughly 75 kcal/mol. The formation of these dislocations and compact low energy (111) patches at very low elongation rate significantly hinders the formation of very long monatomic chains, leading to the final junction structure with only 1- or 2-atom monatomic chains. At elevated 300 K, it appears that the rate-dependent energy release mechanism also applies. When the elongation rate is decreased to 0.05 m/s, we frequently obtain very thick junctions before break (in other words, the formation of monatomic chain becomes a rare event) (see the Supporting Information). However, when the elongation rate is increased to 5 m/s, we obtain a very long, 15-atom monatomic chain, as shown in Figure 7 (in this extreme case, the Au−Au bond length in the single-atomic chain is found to vary from 2.4 to 3.0 Å). The packing structures at the two end contacts of this monatomic chain are much more disordered. The total energy of this elongated structure is 291.2 kcal/mol higher than the thick junction structure obtained at 0.05 m/s. These observations indicate that the formation of high energy, very long monatomic chains is favored if the elongation rate is sufficiently high.

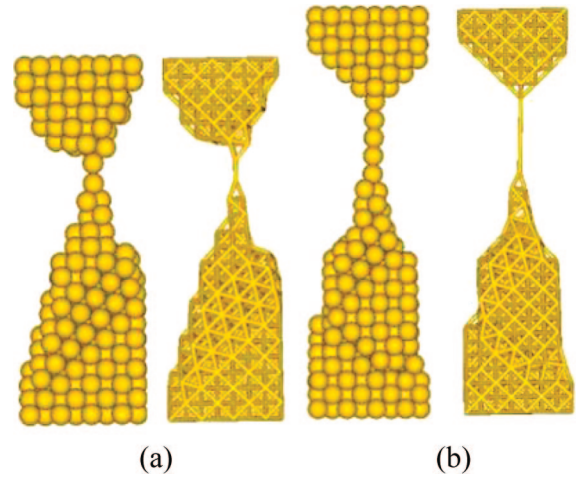

Figure 6. Au256 monatomic chains formed at 0.01 K with elongation rates of (a) 0.05 and (b) 1.0 m/s, respectively. The formation of a 2-atom short chain at 0.05 m/s is accompanied by (111) reconstructions of the original (100) facets and well-defined dislocation lines at the boundary between (111) and (100) facets. The stick presentation shows more clearly the six-coordinated atoms in (111) patches. This is in contrast to Figure 6b, where less (111) patches are formed when the elongation rate is increased to 1 m/s.

Similar to the elongation of Au256, we observe the same elongation phenomena for Au448 at 0.01 K. Very long monatomic chains at high elongation rate (1.0 m/s) and very short monatomic chains at low elongation rate (0.05 m/s) are frequently obtained. The histogram in Figure 3 shows that at 1.0 m/s elongation rate, the probabilities of the occurrence of 6- and 13-atom long monatomic chains become very high. The formation of these very long single-atom chains for Au448 is obviously associated with the longer relaxation times of low energy defects for Au448, since more gold atoms have been involved in the dynamic process. On the other hand, at low

(36) Bahn, S. R.; Jacobsen, K. W. *Phys. Rev. Lett.* **2001**, *87*, 266101.
(37) Novaes, F. D.; da Silva, A. J. R.; da Silva, E. Z.; Fazzio, A. *Phys. Rev. Lett.* **2006**, *96*, 016104.
(38) Legoas, S. B.; Galvao, D. S.; Rodrigues, V.; Ugarte, D. *Phys. Rev. Lett.* **2002**, *88*, 076105.

Figure 7. At 300 K, very long monatomic chain is formed for Au256 when the elongation rate is increased to 5 m/s. The disordered structure at the two end contacts of the monatomic chain also indicates the high energy state of this structure.

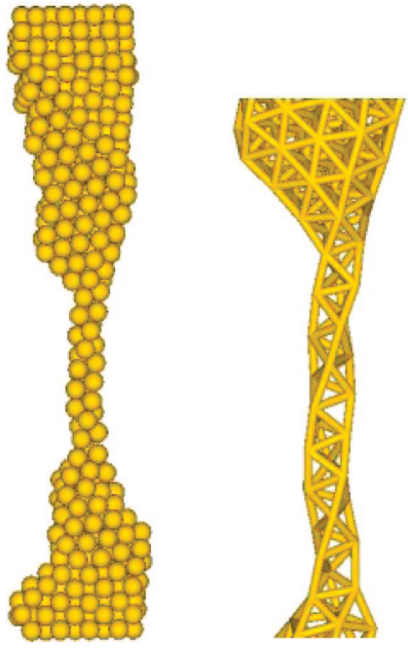

Figure 8. Three-atom-thick helical structure obtained for Au448 at 300 K and under 0.05 m/s elongation rate. The stick presentation clearly shows the (111) reconstructed patches on the two end contacts and the six-coordinated environments for the helical chain.

elongation rate (0.05 m/s, see Figure S1 in the Supporting Information), 1- or 2-atom monatomic chains are frequently obtained. The energy difference between the 13-atom and 1-atom monatomic chains can be as high as ~230 kcal/mol. The same is true at elevated 300 K. We find that under 1.0 m/s elongation rate (Figure 3), most of the junction structures of Au448 exhibit 1- or 2-atom monatomic chains (these are already low energy states due to the fast thermal relaxation of the system). When the elongation rate is decreased to 0.05 m/s, the junction structure adopts a new helical structure. In Figure 8, we see that very large (111) patches are formed on the two contacts of the helical chain. The 3-atom thick helical structure makes each atom in the chain have a coordination number of six, indicating that this helical structure is much more stable than the monatomic chains.

The underlying mechanism of the system size, temperature, and stretching rate effects on the dynamic elongation behavior of gold nanowires can be universally explained by the rate-dependent energy release mechanism that integrates the thermodynamic relaxation properties of gold nanowires. First, as more gold atoms being involved in the elongation of Au nanowire, the relaxation times of many low energy defect modes of the system will increase. The slowing-down of these relaxations would be likely to make the elongation rate exceed the characteristic relaxation rates (the inverse of relaxation times) of the system, thus favoring the formation of high energy monatomic chains. Second, increasing the temperature will usually increase the thermal motions and diffusions of particles, leading to the acceleration of the relaxations of many low energy defect modes of the system. Consequently, the fast thermal motion favors low energy defects initiations, such as well-defined dislocations, surface (111) reconstructions, and the formation of long helical structures. Third, as we discussed before, the very low elongation rate will aid the formation of low energy defects, rather than the formation of high energy, single-atom monatomic chains.

The proposed rate-dependent energy release mechanism essentially indicates that a gold nanowire containing very long monatomic chain would not be mechanically stable at long time scales and high temperatures,[10,11,19] since the system always seeks to decrease its free surface energy over macroscopic timescales. This mechanism, derived from comprehensive MD simulations, thus explains and unifies early observations and speculations about the stability of monatomic chains[10,19] and dramatic different elongation behaviors at different elongation rates.[11] It is now becoming clear that the formation of long single-atomic chain is not a simple issue of how strong the Au−Au bonds in the chain compared to other bonds in the region close to the chain;[36] rather, the formation of this monatomic chain completely depends on the responses of many low energy defect modes in a wide spectrum in the system when a dynamic external load applies.

5. Conclusion

Comprehensive molecular dynamics simulations of the elongation of Au (001) nanowires reveal that the formation of long monatomic chains is favored for longer gold nanowires at low temperatures with high elongation rate. Otherwise, low energy defects, such as very short monatomic chains, thick helical chain structures, surface dislocations, and (111)-patch reconstructions will be more likely to be initiated. These phenomena can be universally explained by the rate-dependent energy release mechanism, which states that when the elongation rate is faster than the characteristic relaxation rates (the inverse of relaxation times) of the low energy defect modes in the system, the formation of very long monatomic chains will be more likely to happen. It appears that these low energy relaxation modes are more complicated and have much longer relaxation times than simple *energy relaxations* induced by a sudden pulling-jump of 0.1 Å, as employed in our previous studies.[25] Recent experimental evidence and theoretical calculations further revealed that incorporation of impurities (light foreign atoms) can enhance the stability of very long gold monatomic chains.[12,21,23,24,37] The effect of these impurities on the rate-

dependent energy release phenomena observed in this study would be an interesting topic in this field.

Acknowledgment. This work was supported by the U.S. Department of Energy (DOE) Office of Science, the Computational Nanoscience project, and also by the National Energy Research Scientific Computing Center (NERSC), which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Supporting Information Available: Detailed counts of the occurrence of monatomic chains for Au256 and Au448 gold nanowires at very low elongation rate (0.05 m/s) and the typical 16 snapshots of Au256 junction structures. This material is available free of charge via the Internet at http://pubs.acs.org.

JA806319G