A Molecular Dynamics Simulation of Multi-wall Platinum Nanowires

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ABSTRACT

Structural formation of platinum (Pt) nanowire (NW) is investigated using the classical molecular dynamics (MD) simulation method. A type of multi-shell Pt NWs is obtained from the simulations. These NWs consist of multi walls formed by rolling fcc (111) triangular network sheets. Experimental evidence of existence of such multi-wall Pt NWs has been reported (Kondo and Takayanagi, Science 289, 606, 2000). The simulations begin from initially random atom configurations. The initial configuration is minimized by the steepest descent method, and assigned a temperature of 601 K with a Maxwell-Boltzmann random distribution. Then simulated annealing is applied such that the temperature of the system is reduced gradually to 1 K and a stable NW structure is obtained. Structural characteristics of these Pt NWs, *i.e.* the lattice parameters, are further examined and presented in this paper.

Keywords: nanowire, molecular dynamics simulation, steepest descent method, periodic boundary condition, velocity verlet algorithm, Berendsen thermostat

1 INTRODUCTION

Metallic nanowire (NW) has been intensively studied in the past decade because of its importance in both fundamental low-dimensional physical theories and technological applications such as nanoelectronic devices. Investigation of configurations and structural properties of the NW is vital for broadening its applications.

Molecular dynamics (MD) simulations have been extensively employed to study metallic NWs. Interest has been paid to several fcc metals such as Au, Cu and Al [1-5]. However, simulations on another important fcc metal - platinum (Pt) - were scarcely reported.

This paper aims to study structural formation of Pt NWs using the classical MD simulation method. A type of multi-shell Pt NWs is obtained from the simulations. These NWs consist of walls formed by rolling an fcc (111) triangular network sheet, featuring different structures than those hexagonal solid Pt NWs which has also been observed in classical MD simulations [6].

Experimental evidence of existence of multi-wall Au NWs and single-wall Pt nanotube has been reported [7-8]. Theoretical investigations have been conducted on such multi-shell NWs of Au [9]. This type of structure was also referred to as helical multi-shell (HMS) NW [7] or cylindrical multi-shell (CMS) NW [10].

Each wall of these multi-shell NWs could be considered as a circular tube formed by folding an fcc (111) triangular network around a chord *OA* and a generatrix *OB*, as shown in Figure 1 where the thicker lines form a unit of unwrapped wire wall. We use the index *IJK* respectively to describe the atom strands in the $[\bar{1}10]$, $[0\bar{1}1]$ and $[\bar{1}01]$ directions of the network. The formed cylindrical wall can be denoted by $n(m)$ in that the wall consists of n atom columns in *K*-direction, the left-handed spiral of the wall consists of m atom rows in *I*-direction and right-handed spiral of n-m rows in *J*-direction. Based on this notation, all tubes other than $n(0)$ and $n(n/2)$ with a even number of n are chiral, and $n(m)$ and $n(n\text{-}m)$ are mirror images of one another [9]. We further use $\alpha\beta\gamma$ for the angles between pairs of the three atom strands. It is obvious that, for an unstrained fcc (111) network, $\alpha = \beta = \gamma = 60^{o}$.

Referring to the notations introduced by Kondo and Takayanagi [7] and Tosatti [9], we use the label n_0-$n_1(m_1)$-$n_2(m_2)$-… to describe the multi-wall NWs consisting of coaxial shells. Besides using n_1, n_2 *etc.* to represent helical atom columns, m_1, m_2 *etc.* are also used to denote the chiral order of each helix wall. $n_0 = 1$ if there is a central strand at the wire axis; otherwise $n_0 = 0$ for a tunnel at the wire axis. For the special case of an ideal 1-$N(0)$ Pt NW in which the radius of the outer wall equals g_0 and the atom distance in the wall is d_{nn}, we can derive $N = 5$ approximately according to the relationship that the perimeter = $Nd_{nn} = 2\pi g_0$. g_0 is the distance between neighboring (111) layers and $g_0 = \sqrt{2/3}\, d_{nn}$.

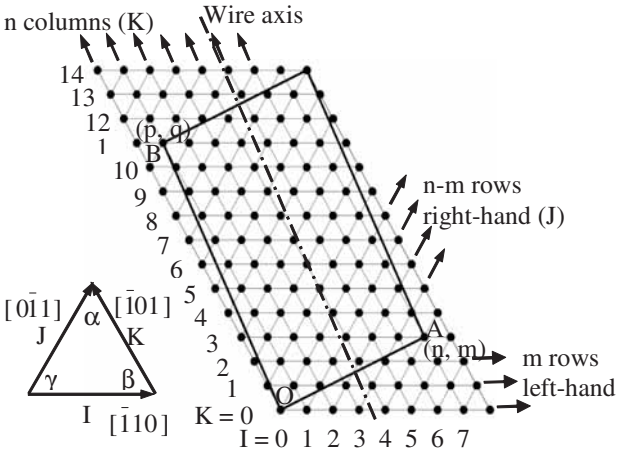


Figure 1: Folding of a triangular network.

2 SIMULATION METHOD

In this work, we investigated structural formation of thin and ultra-thin Pt NWs using a classical MD simulation. Interactions between Pt atoms were described by the Sutton-Chen many body potential [11], which was a development of one first proposed by Finnis and Sinclair [12]. The potential energy of an atomic system is written as:

$$V = \varepsilon\left[\sum_{i>j}\left(a_0/r_{ij}\right)^n - c\sum_i \rho_i^{1/2}\right] \quad (1)$$

where a_0 is the lattice parameter, r_{ij} the distance between atoms i and j and ρ_i local particle density, given by

$$\rho_i = \sum_{i>j}\left(a / r_{ij}\right)^m \quad (2)$$

The exponents n and m determine the range and shape of the potential and the parameters ε and a_0 determine the scales of energy and length respectively. The constants in the potential for Pt taken from [11] are ε = 19.83 meV, c = 34.408, m = 8, n =10 and the lattice parameter a_0 = 3.92 Å. The interaction between atoms was truncated in the simulation at $2.7d_{nn}$ where d_{nn} is the nearest-neighbor distance and $d_{nn} = a_0/\sqrt{2}$ = 2.772 Å. Another important parameter is the distance g_0 between neighboring (111) layers and $g_0 = a_0/\sqrt{3}$ = 2.263 Å for Pt.

The Newton equations of the MD were integrated using the velocity Verlet algorithm [13] with a timestep Δt = 2 fs. To control temperature, the Berendsen thermostat [14] was applied with a characteristic relaxation time of 2.5 ps.

In the simulations, a periodic boundary condition (PBC) was considered in the axial direction of the NWs to simulate wires with infinite length. The simulations begin with initial configurations consisting of random distributions of atomic positions. Initial configurations of the Pt NWs were obtained by randomly arranged positions of atoms with a criterion that the nearest atom distance is 2.3 Å. This distance criterion is a compromise between feasibility of randomly generating the positions and a reasonably confined volume of the initial configuration. As this distance is much smaller than the lattice nearest-neighbor distance d_{nn}, a minimization procedures was first carried out by the steepest descendent method (SDM) to relax the initial configurations.

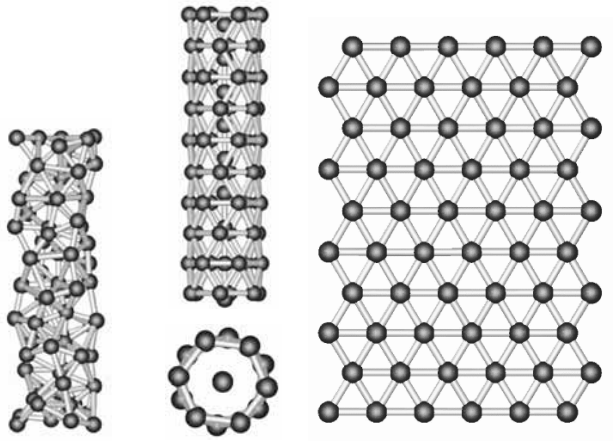
After minimization, simulated annealing was performed. The NWs were first assigned a temperature of 601 K and velocities of atoms were specified with a Maxwell-Boltzmann random distribution. Then the MD simulation runs 200 cycles. In each cycle, the temperature was reduced 3 K in the first step followed by 9999 steps with temperature control. Therefore the simulation time for each cycle is 20 ps and this simulated annealing phase lasted 4 ns. The initial temperature of 601 K is chosen so that the final temperature is approximately 1 K instead of 0 K whereby temperature control would encounter numerical singularity. When the phase finished, configurations of the NW became stable.

However, force in the NW along the axial direction may not equal to zero. So an MD simulation phase was further executed with 50 cycles to achieve a zero-stress state in the NWs. At the first step in each cycle, the residual force in the NW was measured from results of previous cycle and the length of the NW was accordingly adjusted. This was followed by 9999 relaxation steps with fixed NW length and temperature control. In all cases, the simulations converged to a stable NW length before 50 cycles finished.

Structural characteristics of these Pt NWs, *i.e.* lattice parameters, are then examined and presented in this paper.

3 RESULTS AND DISCUSSION

Figures 2-4 illustrates three single-wall NWs consisting of 69, 77 and 84 atoms, denoted as 1-6(0), 1-7(4) and 1-6(1) respectively. The final lengths of the NWs are always shorter than the initial ones. The atom distances in the central strands are smaller than d_{nn}, indicating the central strands are in a compressed state. With over five atom columns in the NWs, the radii of the outer walls are all greater than g_0, which should be in a 1-5(0) Pt NW as discussed in Section 2. The atom distances in the outer walls except d_1 of the 84-atom NW are smaller than d_{nn}. Deviation of the atom bond angles from 60° shows the outer walls being distorted and excessive distortion of the 84-atom NW leads to $d_1 > d_{nn}$.



(a) (b) (c)

Figure 2: Configuration of a 1-6(0) Pt NW with 69 atoms: (a) initial; (b) final side and top views; (c) unwrapped outer wall. The NW has initially a length of 23.2 Å and finally 23.09 Å. The average neighboring atom distance in the central strand d_0 = 2.564 Å. The outer wall has a radius of 2.617 Å and the neighboring atom distance d_1 = 2.741 Å and $d_J = d_K$ = 2.687 Å. The atom bond angle α = 61.34° and $\beta = \gamma$ = 59.33°.

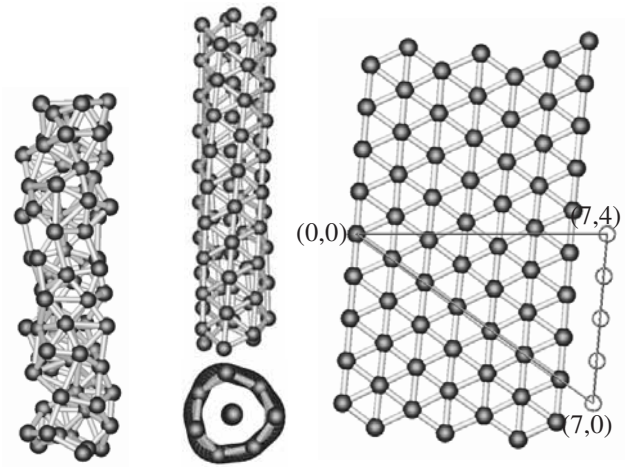


Figure 3: Configuration of a 1-7(4) Pt NW with 77 atoms: (a) initial; (b) final side and top views; (c) unwrapped outer wall. The NW has initially a length of 26.4 Å and finally 25.72 Å. The average neighboring atom distance in the central strand d_0 = 2.572 Å. The outer wall has a radius of 2.616 Å and the neighboring atom distance d_I = 2.688 Å, d_J = 2.711 Å and d_K = 2.699 Å. The atom bond angle α = 59.65°, β = 60.39° and γ = 59.96°. The open circles represent mirror images of atoms for assisting observation of the parameters $n_1(m_1)$.

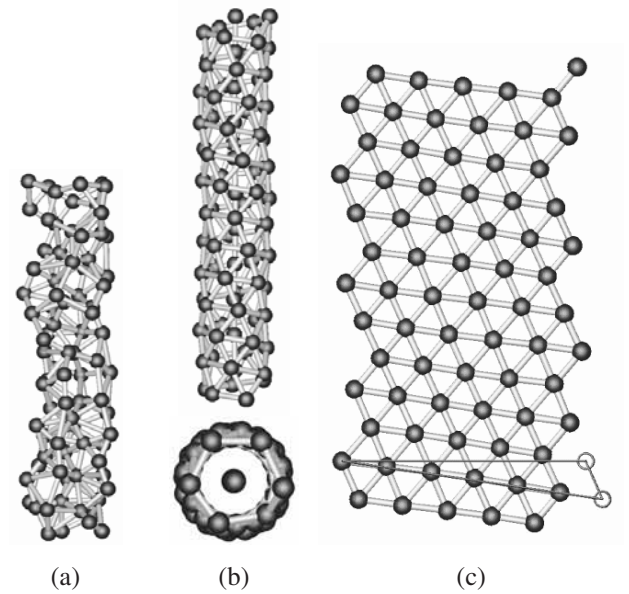


Figure 4: Configuration of a 1-6(1) Pt NW with 84 atoms: (a) initial; (b) final side and top views; (c) unwrapped outer wall. The NW has initially a length of 30 Å and finally 29.41 Å. The average neighboring atom distance in the central strand d_0 = 2.674 Å. The outer wall has a radius of 2.541 Å and the neighboring atom distance d_I = 2.872 Å, d_J = 2. 666 Å and d_K = 2.653 Å. The atom bond angle α = 65.34°, β = 57.59° and γ = 57.07°.

Figure 5 shows a double-wall 1-6(2)-12(2) Pt NW with 177 atoms. Again, the lengths of the final configurations are smaller than the initial and the atom distances in the central strands are smaller than d_{nn}. Though the radius of the inner wall is greater than g_0, the distance between the inner and outer walls is quite close to g_0. The inner wall is in excessive distortion leading to both d_I and d_J greater than d_{nn}. Distortion of the outer wall is not so intensive and only d_K is greater than d_{nn}.

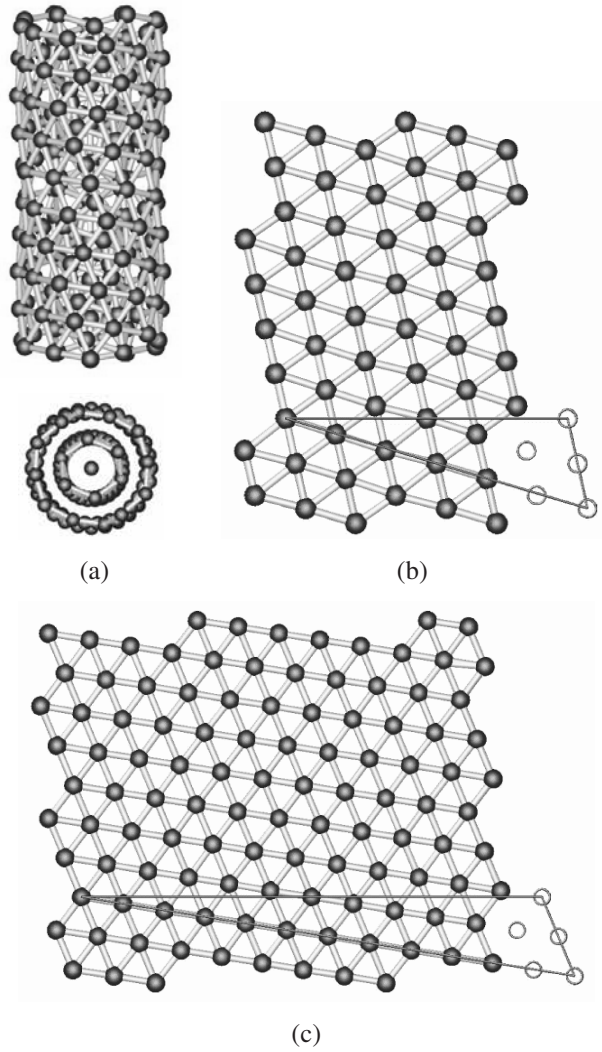


Figure 5: Configuration of a 1-6(2)-12(2) Pt NW with 177 atoms: (a) final side and top views; (b) unwrapped inner wall; (c) unwrapped outer wall. The NW has initially a length of 24.6 Å and finally 23.94 Å. The average neighboring atom distance in the central strand d_0 = 2.661 Å. The inner wall has a radius of 2.572 Å and outer wall 4.764 Å, thus a distance of 2.192 Å between them. The neighboring atom distance of the inner wall d_I = 3.011 Å, d_J = 2.870 Å and d_K = 2.630 Å and the atom bond angle α = 66.26°, β = 60.88° and γ = 52.86°; and outer wall d_I = 2.706 Å, d_J = 2.672 Å and d_K = 2.779 Å and the atom bond angle α = 59.51°, β = 58.30° and γ = 62.18°.

Figure 6 shows a triple-wall 1-6(4)-12(8)-18(14) Pt NW with 333 atoms. The atom distance in the central strand of this NW mostly approaches d_{nn} among the five simulated NWs, though still smaller than d_{nn}. The radius of the inner wall is still greater than g_0, but the distances between the inner and middle walls and between the middle and outer walls are quite close to g_0. Some faults exist in the NW. The inner wall has two atom columns in dislocation as indicated by two dashed lines; it is therefore not a pure (111) triangular network. That is why the average atom distances at all the three *IJK* directions in this wall are greater than d_{nn}. There are cavities in the middle and outer walls. The middle wall is intermediately distorted so that d_I and d_K are smaller than but $d_I > d_{nn}$. The outer wall is only slightly distorted and all the atom distances are smaller than d_{nn}.

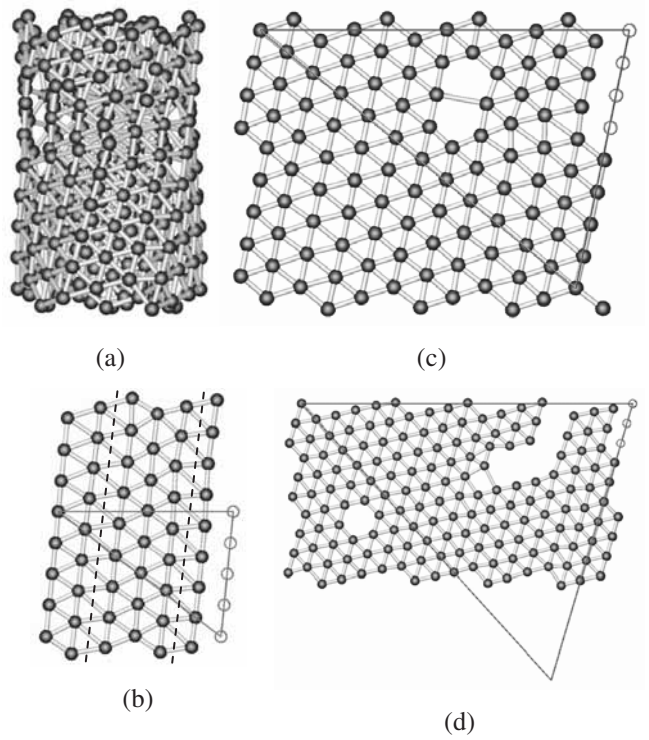


Figure 6: Configuration of a 1-6(4)-12(8)-18(14) Pt NW with 333 atoms: (a) initial; (b) unwrapped inner wall; (c) unwrapped middle wall; (d) unwrapped outer wall. The NW has initially a length of 25 Å and finally 24.28 Å. The average neighboring atom distance in the central strand d_0 = 2.708 Å. The inner wall has a radius of 2.502 Å, middle wall 4.739 Å and outer wall 6.962 Å, thus distances of 2.237 Å and 2.223 Å between them. The neighboring atom distance of the inner wall d_I = 2.814 Å, d_J = 2.907 Å and d_K = 2.811 Å and the atom bond angle α = 65.23°, β = 60.97° and γ = 53.80°; middle wall d_I = 2.753 Å, d_J = 2.804 Å and d_K = 2.656 Å and the atom bond angle α = 60.45°, β = 62.44° and γ = 57.11°; and outer wall d_I = 2.717 Å, d_J = 2.680 Å and d_K = 2.696 Å and the atom bond angle α = 60.48, β = 59.44° and γ = 60.08°.

4 CONCLUSIONS

An MD study of the Pt NW was conducted. Beginning from random configurations of NWs, the simulations included a minimization procedure followed by simulated annealing with a thermostat algorithm. Five simulated Pt NWs are reported in this paper. Though geometric consideration of a Pt (111) triangular sheet dictates five atom columns for a single wall Pt NW, our simulations obtained NWs with six or seven columns in the single wall or inner wall, and a difference of six atom columns between each pair of walls in multi-wall NWs. By unwrapping the walls, structural parameters of the NWs are measured. Radii of the inner wall are always greater than the distance between (111) layers in bulk Pt, but the distance between the walls are quite close to that parameter. Atom distances in central strands and walls are smaller than the bulk lattice parameter except in cases where the walls are excessively distorted.

REFERENCES

[1] G. Bilalbegovic, Comp. Mater. Sci. 18, 333, 2000.
[2] G. Bilalbegovic, J. Phys. Condens. Mat. 13, 11531, 2001.
[3] J.W. Kang and H.J. Hwang, Nanotechnology 12, 295, 2001.
[4] J.W. Kang and H.J. Hwang, Mol. Simul. 28, 1021, 2002.
[5] A. Hasmy, P.A. Serena and E.Medina, Mol. Simul. 29, 427, 2003.
[6] Q.H. Cheng, C. Lu and H.P. Lee, Mol. Simul., in press, 2005.
[7] Y. Kondo and K. Takayanagi, Science 289, 606, 2000.
[8] Y. Oshima, H. Koizumi, K. Mouri, H. Hirayama, K. Takayanagi and Y. Kondo, Phys. Rev. B 65, 121401, 2002.
[9] E. Tosatti, S. Prestipino, S. Kostlmeier, A. Dal Corso and F.D. Di tolla, Science 291, 288, 2001.
[10] J.W. Kang and H.J. Hwang, Comput. Mater. Sci. **27**, 305, 2003.
[11] A.P. Sutton and J. Chen, Phil. Mag. 61, 139, 1990.
[12] M.W. Finnis and J.E. Sinclair, Phil. Mag. 50, 45, 1984.
[13] M.P. Allen and D.J. Tildesley, "Computer Simulation of Liquids," Clarendon Press, Oxford 1987.
[14] H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren, A. DiNola and J.R. Haak, J. Chem. Phys. 81, 3684, 1984.

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