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Molecular dynamics study on mechanics of metal nanowire

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Abstract

The new concept of using nanowires as building blocks for logic and memory circuits makes it very necessary to fully understand the mechanical behaviors of these nanowires. Embedded-atom method is employed to carry out three-dimensional molecular dynamics simulations of the mechanical properties of rectangular cross-section copper nanowire. A stable free-relaxation state and the stress–strain relation of nanowire under extension are obtained. The elastic modulus, yielding strength and deformation are studied. The surface effect, size effect, and temperature effect on the extension property of metal nanowire are discussed in detail. The simulation results from our present work show that at nanoscale surface atoms play an important role on the mechanical behaviors of nano-structures. This study of mechanical properties of metal nanowires will be helpful to the design, manufacture and manipulation of nano-devices.

Keywords: Molecular dynamics simulation; Metal nanowire; Mechanical behavior

1. Introduction

With the fast development of nano science and technology (NST), the idea of assembling electronic circuits from molecular-scale devices has recently gained increasing interest. Nanoelectromechanical systems (NEMS) (Craighead, 2000) are evolving, with new scientific studies and technical applications emerging. Mechanical devices are shrinking in thickness and width to reduce mass, increase resonant frequency, and lower the force constants of these systems. Metal nanowires are important components of nanoscale devices. By etching a cleaved molecular-beam epitaxy grown substrate, a robust technique for fabrication of extremely narrow metal wires with controlled widths substantially below 10 nm was developed by Natelson et al. (2000). The thinnest metal Au nanowire with only four atomic rows was successfully

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prepared by Kondo and Takayanagi, using electron-beam irradiation in an ultrahigh vacuum electron microscope (Kondo and Takayanagi, 1997). Recently, the concept of nanowires as building blocks for self-assembling logic and memory circuits was presented by Kovtyukhova and Mallouk (2002).

Owing to the progress of techniques and technology with high performance and high efficiency, fundamental understanding of their phenomena and functions from the elementary processes of molecular motion has increasingly been required. This leads to the introduction of "molecular mechanical engineering", which forms a bridge between microscopic molecular understanding and macroscopic continuum engineering, i.e. molecular science and mechanical engineering (Kotake, 1995). Microscopic understanding of phenomena surely leads to elucidation of the fundamental mechanisms, and further it may yield a solution to problems inexplicable or inaccessible from the macroscopic viewpoint, and a breakthrough in the development of mechanical engineering technology in the future. As mechanics is the base of mechanical engineering, nano-mechanics will play an important role in the development and application of molecular mechanical engineering, which is mainly on the design, manufacture and manipulation of molecular machines. Using molecular mechanics and molecular dynamics analysis, Cagin et al. studied the molecular nanomachine designs pioneered by Drexler and Merkle, and optimized the structures of the two planetary gear designs and the neon pump (Cagin et al., 1998). This can be considered as an extension to nanoscale of traditional computer-aided engineering. We can name it as molecular computer-aided engineering (MCAE).

Metallic nanowires have received considerable attention in recent years, especially numerical simulation study. Theoretical work has been carried out mainly by employing the molecular dynamics method (Kang and Hwang, 2001; da Silva et al., 2001; Mehrez and Ciraci, 1997; Ikeda et al., 1999; Wang et al., 2001; Wu, 2004) or direct simulation Monte Carlo method (Tanimori et al., 1999). The latter ignores the molecular collision kinetics and assumes some statistical or Monte Carlo probabilities, but it has an advantage in treating large time scale. The former is more straightforward and can elucidate the details of deformation evolution by motion of atoms. Previous works are mainly on the mechanism of deformation and fracture, and some good results are obtained. However, some improvements and progresses can still be made. Boundary conditions can be more realistic and accurate so as to minimize the boundary effects. Atomistic stress can be introduced, which will connect the macro mechanics concepts and micro atomic motions well. More attention needs to be paid to the initial relaxation state of nanowire.

In this paper, a three-dimensional molecular dynamics study on metal nanowire is presented, especially from the view point of mechanics. The free-relaxation state is first studied, and surface effect is discussed. Then extension properties of copper nanowire are simulated. Size effect and temperature effect are investigated. Finally, some conclusions are made.

2. Modeling and simulation

Rectangular nanowires cut from bulk single crystal copper, as Fig. 1 shows, are simulated. The initial atomic configuration is positioned at the fcc lattice sites. The X, Y, Z coordinate axes represent the lattice

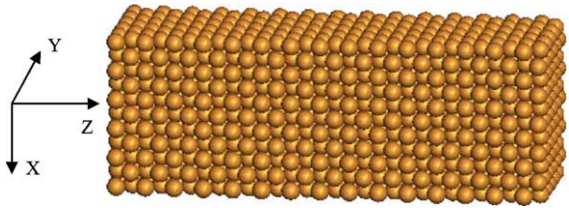

Fig. 1. Simulation cell of copper nanowire.

direction of [1 0 0], [0 1 0], [0 0 1] respectively. Periodic boundary condition is applied in the length direction, i.e. Z direction. The surfaces in X and Y directions are free. The existence of free surfaces will result in the relaxation motion of atoms near the surface, which will then minimize the total potential energy of the system.

An embedded atom potential of copper, proposed by Doyama and Kogure (1999), has been employed to represent the atomic interactions. The potential parameters are determined from the experimental data. The classic algorithms, such as potential table, force table, and neighbor atom list, are implemented to calculate the interaction forces. In each simulation the temperature is kept constant by using a direct velocity scaling method. The gear algorithm of fifth time derivative of the atom position is used to integrate Newton's equations of motion. The time-step is dependent on the simulation temperature and loading rate, from 10 fs to 0.2 fs.

After full relaxation, extension strain loadings are applied by uniformly scaling the z coordinates. The atoms of the outermost layer at each end are only constrained in the z direction during each loading step. The step-wise tensile strain is 0.001–0.0001. It is relaxed for some time in each step. Both the strain step and relaxation time determine the strain rate. This step of tension/relaxation is repeated until the material fails or the total strain reaches some extent. The stress in the nanowire under above strain loading is computed using Virial method. There are some controversies about using this method to compute the normal stress of a free surface.

The atomistic stress is expressed in terms of EAM potential functions as Eq. (1). The functions of, V, F, Φ are empirical functions with parameters from Doyama and Kogure (1999). r_{ij} is the distance between atom i and atom j. ρ_i is electron cloud density. α, β are Cartesian coordinates. Ω is the volume of an atom. v_i^α is the velocity in α direction of atom i. The first and second parts represent thermal contribution and atomic interaction contribution respectively.

$$\sigma^i_{\alpha\beta} = \frac{1}{\Omega^i}\left\{-mv_i^\alpha v_i^\beta + \frac{1}{2}\sum_{j\neq i}\left[\frac{\partial V}{\partial r_{ij}} + \left(\frac{\partial F}{\partial \rho_i} + \frac{\partial F}{\partial \rho_j}\right)\frac{\partial \Phi}{\partial r_{ij}}\right]\frac{r_{ij}^\alpha r_{ij}^\beta}{r_{ij}}\right\}. \tag{1}$$

3. Results and discussion

3.1. Free relaxation

Due to the creation of new free surfaces, the atoms on and near surfaces will lose some neighbor atoms and electronic density. This will destroy the balance of these atoms and lead to their motion without external loading, which is so called free relaxation. Periodic boundary condition is applied in the length direction. During the relaxation simulation, the pressure in the length direction is kept constant at zero by using Anderson constant pressure algorithm (Andersen, 1980). It is found that the length of nanowire contracts about 2.57% for the cross-section of $5.5a \times 5.5a$ (a is the lattice constant of copper, which is 0.3609 nm), compared with the single crystal bulk. Here we use half lattice constant for cross-section to make it symmetrical, but for length direction, the size is integer times of lattice constants, otherwise the periodic boundary will result in problems.

The loss of neighboring atoms and electronic density can also lead to the high energy of surface atoms (Wu, 2004). Energy is an important characteristic parameter to describe the mechanical properties of materials, so it is expected that surface atoms will have a different property and will play an important role on the mechanical behaviors of nano-structured materials.

Fig. 2 shows the stress distribution at cross-section of nanowire after free relaxation. It is found that not only surface stress of extension exists near and on surface of nanowire, but also compression stress exists

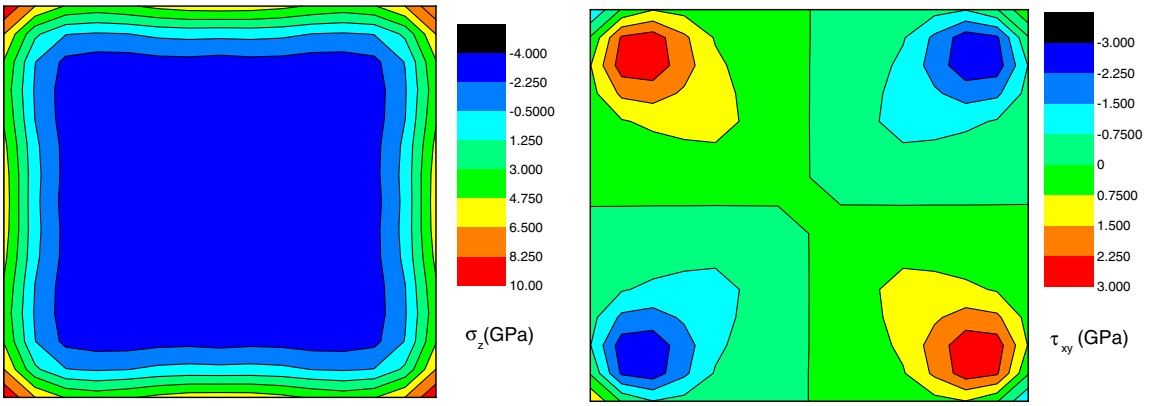

Fig. 2. Atomic stress distribution at cross-section of loading-free nanowire.

inside the nanowire. These are self-balanced stresses, i.e. the total stress is zero because there is no external loading during free-relaxation process. The magnitude of these stresses is remarkable, at orders of GPa. This pre-stresses state will have big influence on the mechanical behaviors of metal nanowire.

3.2. Stress–strain curves

The simulation cell is $5.5a \times 5.5a \times 15a$. Period boundary condition is only applied in the length directions (z). The simulation temperature is 1.0 K. The tensile strain step is 0.0001 until the nanowire breaks up. To get the total stress, we use the average of all atomistic stress by weight of Voronoi volume of atoms. The stress–strain curve of simulation nanowire under tensile strain is shown in Fig. 3. The strain of first yielding point is 0.153, higher than that of single crystal copper bulk.

Before the first peak point, the stress–strain curve is approximately linear. The fitted extension modulus is 75.4 GPa, lower than that of single crystal copper bulk, which is about 85 GPa. After reaching the peak value, the stress goes down dramatically. The peak stress is defined as yielding stress. From the figure, there

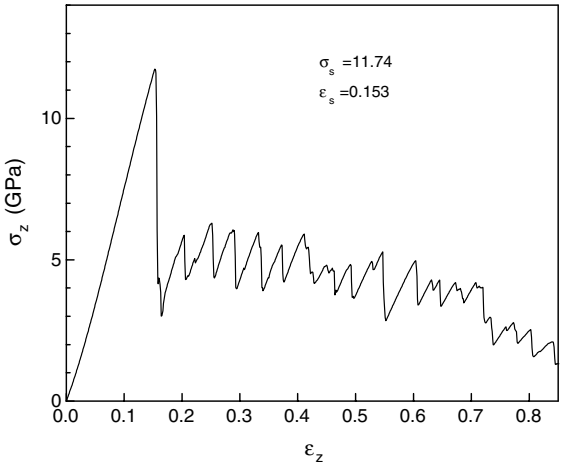

Fig. 3. Stress–strain curve.

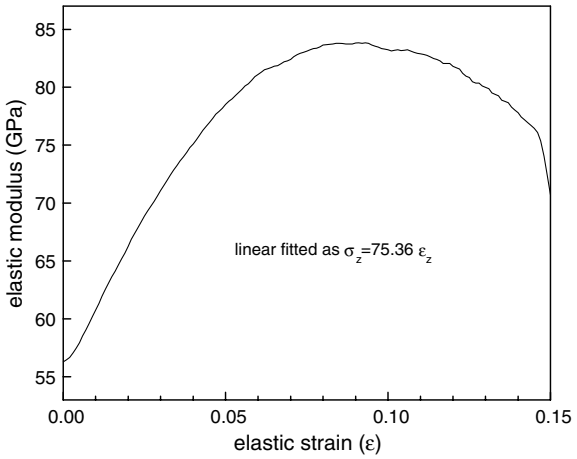

Fig. 4. Extension modulus varying with strain.

is no strain-hardening for copper nanowire, so the yielding stress can be considered as stress strength. The deformation before yielding is elastic. The following deformation is plastic. Plasticity comes from dislocations, and the emission and movement of different dislocation systems results in saw-like curve. The break-up strain is 0.85.

In elastic stage of above curve, the extension modulus can also be obtained by derivation calculus of stress to strain. Fig. 4 shows the curve of extension modulus with elastic strain. It is found that modulus is not constant from the strain range of 0–0.15. The variation may come from the inhomogeneity of cross-section of nanowire, which is resulted from surface effect. Stress distribution across section is not uniform, and the distribution varies with extension strain. Fig. 5 shows the distribution of stress in extension direction at cross-section with strain of 9% and 15%. The stress in inner part of nanowire is still compression under small extension strain. At small strain, the high-stress regions are only at corners. At large strain, the high-stress regions are only at the middle of edges. At strain of 9%, the high-stress regions are corners and middle edges, which make this strain state more powerful to undertake extension loading. This is why the elastic modulus reaches highest value at strain of 9%.

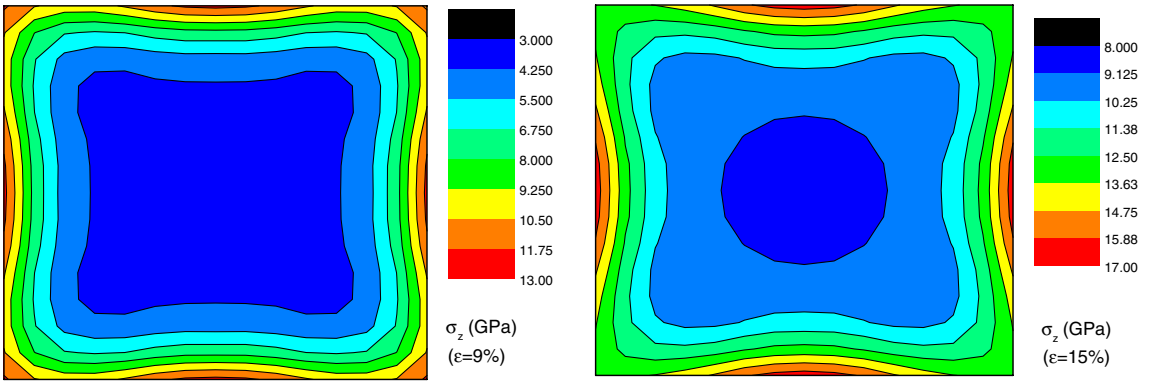

Fig. 5. Contour of stress evolvement with extension.

3.3. Size effect

Copper nanowires with various sizes of cross-section were simulated for comparison. All of the nanowires have the same aspect ratio, 1:1:3, with periodic boundary condition in length direction. The cross-section sizes are from 1.62 nm to 9.18 nm (from 4.5*a* to 25.5*a*). Fig. 6 shows the stress–strain curve for different sizes. Fig. 7 shows the elastic modulus and yielding stress varying with sizes of cross-section, where the modulus is the average modulus of the elastic stage.

It is found that the mechanical properties of metal nanowire are considerably size-dependent. The elastic modulus decreases with increasing size of cross-section, while yielding stress increases with increasing size of cross-section. Atomistic effects are clearly evident for nanowire with cross-section size less than 10 nm. The elastic modulus of copper nanowire is lower than that of single crystal copper bulk. With the increasing size of cross-section, the elastic modulus of nanowire converges to that of bulk, and also the yielding strength of

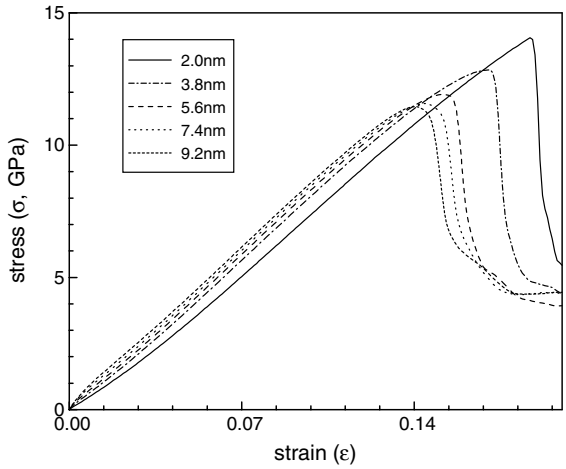

Fig. 6. Stress–strain curve for different sizes of cross-section.

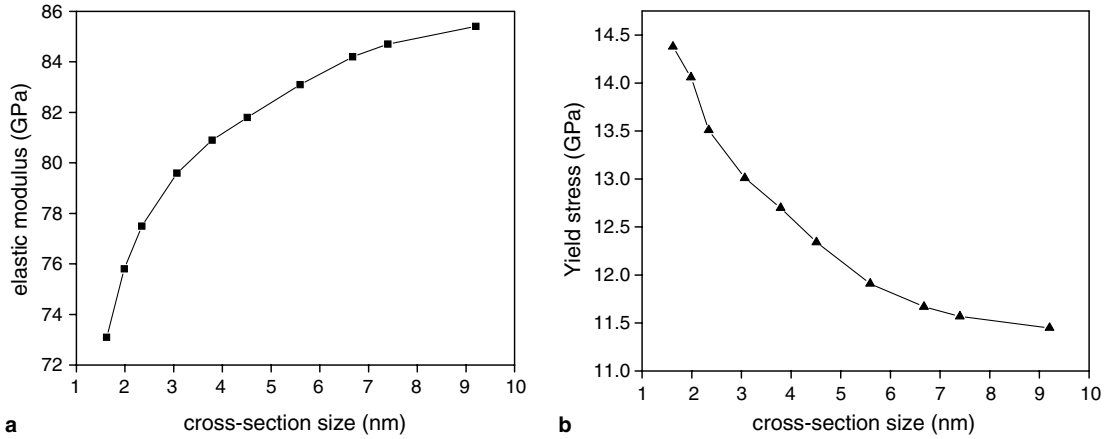

Fig. 7. (a) A plot of the Young's modulus as a function of cross-section size of nanowire. (b) A plot of yielding stress as a function of cross-section size of nanowire.

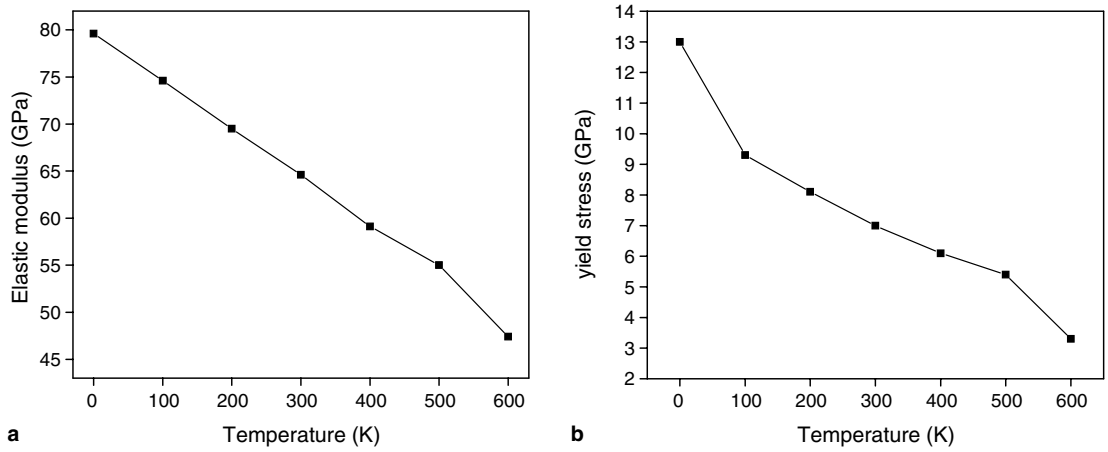

Fig. 8. (a) Plot of elastic modulus of copper nanowire as a function of temperature. (b) Plot of yielding stress of copper nanowire as a function of temperature.

nanowire converges to that of bulk. We owe size effect to surface effect essentially. The ratio of surface atoms to totality increases with decreasing length size for materials and structures. The surface atoms include two to three layers of atoms, not only the outmost one layer.

3.4. Temperature effect

Conceptually, temperature in macroscale comes from atomic motions in microscale. At non-zero temperatures, atoms in metal crystals move due to thermal oscillations around the equilibrium positions besides the motions due to external force. Computer simulation using atomistic models provides a valuable tool for investigating dynamical processes at non-zero temperatures. Although its limit of length size and time scale, we can use it to gain insight into the microscopic basis of macroscopic phenomena. We studied the extension properties of copper nanowires at different temperatures from 0 K to 600 K. Fig. 8 shows the curves of elastic modulus and yielding stress with temperatures. The simulation cell is $5.5a \times 5.5a \times 15a$, and period boundary condition is only applied in length directions.

It is interesting that from temperatures of 100 K to 500 K, elastic modulus and yielding stress of copper nanowire decrease approximately linearly with increasing temperature. This is the thermal-softening effect. The above two material constants vary significantly with temperature, but at middle temperatures they both vary linearly, so in fact the yielding strain does not vary with temperature remarkably.

4. Summary

In our present work, molecular dynamics simulations have been carried out to investigate the mechanical behaviors of copper nanowire. Self-balanced stresses exist in the nanowire, extension near and on surfaces and compression inside, which is due to surface effect. Surface atoms play an important role in the mechanics of nanowire. The stress–strain relation of nanowire is obtained by numerical simulations. The size effect and temperature effect on the extension properties are discussed in detail. The simulation results show that the mechanical properties at nanoscale are different from those at macroscale. Study on the mechanical properties of metal nanowires can give us more fundamental understanding of nanoscale machines from

atomistic motions. The investigation on the configuration, stress, elasticity, yielding and deformation will contribute to the design, manufacture and manipulation of nano-devices.

Acknowledgements

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