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The elastic properties and energy characteristics of Au nanowires: an atomistic simulation study*

Liu Shan-Shan(刘珊珊), Wen Yu-Hua(文玉华)†, and Zhu Zi-Zhong(朱梓忠)

Department of Physics, and Institute of Theoretical Physics and Astrophysics, Xiamen University, Xiamen 361005*, China*

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This paper have performed molecular static calculations with the quantum corrected Sutten–Chen type many body potential to study size effects on the elastic modulus of Au nanowires with [100], [110] and [111] crystallographic directions, and to explore the preferential growth orientation of Au nanowires. The main focus of this work is the size effects on their surface characteristics. Using the common neighbour analysis, this paper deduces that surface region approximately consists of two layer atoms. Further, it extracts the elastic modulus of surface, and calculate surface energy of nanowire. The results show that for all three directions the Young's modulus of nanowire increases as the diameter increases. Similar trend has been observed for the Young's modulus of surface. However, the atomic average potential energy of nanowire shows an opposite change. Both the potential and surface energy of [110] nanowire are the lowest among all three orientational nanowires, which helps to explain why Au nanowires possess a [110] preferred orientation during the experimental growth proceeds.

Keywords: nanowire, elastic modulus, size effect, molecular static approach
PACC: 6146, 6220, 7115Q

1. Introduction

In recent years, one-dimensional nanowires (NWs) have attracted a great deal of interests due to their potential applications in nanoelectronic, optoelectronic and nanoelectromechanical systems.[1,2] The functionalities and applications of nanowires greatly depend on their mechanical properties. To date, some experimental measurements, such as scanning electron microscopy, transmission electron microscopy, and atomic force microscopy have investigated the mechanical responses of nanowires, which have been deduced to different results.[3−8] For example, some experiments show that the Young's moduli of ZnO, Ag and Pb nanowires decrease dramatically with decreasing diameter,[3,4] whereas Si and Cr nanowires show an opposite tendency.[5,6] Especially for SiC and Au nanowires, their Young's moduli are essentially independent of diameter.[7,8] But the results obtained from experiments are easily influenced by a variety of factors such as environment and the quality of samples. Many other researchers try to avoid these affections by computer simulations in stead of by experiments, and have studied kinds of nanowires and deduced various results about elastic properties. Theoretically, molecular dynamics (MD) simulations have shown that Cu and Au nanowires exhibit softening along $< 100 >$ and $< 111 >$ directions, while Cu nanowire exhibits stiffening along $< 110 >$ direction,[9,10] which due to the nonlinear elasticity of core. Similar trends have been observed in MD simulations of Cu and Al thin films.[11,12] These developments have prompted renewed interest in exploring the shape effects on elastic properties of those nanowires.

Gold metal possesses many excellent properties, such as good electrical and thermal conductivity, high ductility and chemical inertness etc., all these characteristics being important for the fabrication and applications of reliable electrical nanocontacts, sensors and spectroscopic probes.[13−15] So, many researchers have paid much attention to explore the physical properties of Au nanowires. Gold has been found to form specially long and stable monatomic chains, observed by high resolution transmission electron microscopy.[13,14] Sakai and co-workers observe experimentally that Au nanowires' Young's modulus increases with decreasing temperature,[15] and other

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†Corresponding author. E-mail: yhwen@xmu.edu.cn

researches find that for Au nanowires with diameter ranging from 40 nm to 250 nm, their Young's modulus are essentially independent of diameter.[8]

It is of vital importance for us to understand the mechanical properties of Au nanowires for better control of their fabrication and functionality. However, characterization of the mechanical properties is a challenge to many existing testing and measuring techniques because of the tiny dimension of nanowires making the manipulation rather difficult. Atomistic computer simulations, usually using semiempirical or empirical approaches to describe interatomic interactions, are an alternative effective way to understand the mechanical behaviour of nanowires.[9−12] In this paper, We address the size effects on the surface characteristics (elastic modulus and energy) of Au nanowires along [100], [110] and [111] crystallographic orientations using molecular static calculation with many-body potential, and further explore the preferential growth orientation of Au nanowires from the viewpoint of energy. This paper is structured as the following. A brief description of the simulation methods is given in Section 2. In Section 3, the elastic and energy characteristics of Au nanowires with different size are analysed, and followed by a detailed discussion on their surface elastic moduli and surface energies. Comparisons with other results are also presented in this section. Finally, the main conclusions are to be summarized in Section 4.

2. Simulation methods

In molecular static calculations, we use the quantum corrected Sutten–Chen (Q–SC) type potentials modified[16] to describe interatomic interactions for metal nanowires. These potentials represent many-body interactions, and their parameters are optimized to describe the lattice parameter, cohesive energy, bulk modulus, elastic constants, phonon dispersion, vacancy formation energy, and surface energy, leading to an accurate description of many properties of metals and their alloys.[17,18] For the SC type force field, the total potential energy for a system of atoms can be written as

$$\begin{aligned} U &= \sum_{i}^{N} U_i \\ &= \sum_{i}^{N} \varepsilon \left[\frac{1}{2} \sum_{j \neq i}^{N} V(R_{ij}) - c\sqrt{\rho_i} \right], \end{aligned} \tag{1}$$

here $V(R_{ij})$ is a pair interaction function defined by the following equation

$$V(R_{ij}) = \left(\frac{a}{R_{ij}} \right)^n, \tag{2}$$

accounting for the repulsion between the i and j atomic cores; ρ_i is a local electron density accounting for cohesion associated with atom i defined by

$$\begin{aligned} \rho_i &= \sum_{j \neq i}^{N} \phi(R_{ij}) \\ &= \sum_{j \neq i}^{N} \left(\frac{a}{R_{ij}} \right)^m. \end{aligned} \tag{3}$$

In Eqs.(1)–(3), R_{ij} is the distance between atoms i and j, a_0 is a length parameter scaling all spacings (leading to dimensionless V and ρ); c is a dimensionless parameter scaling the attractive terms; ε sets the overall energy scale; n and m are integer parameters such that $n > m$. Given the exponents (n, m), c is determined by the equilibrium lattice parameter, and ε is determined by the total cohesive energy. For the Q-SC type potential of Au, the parameters are given as follows: $n = 11$, $m = 8$, $\varepsilon = 7.8052$ meV, $c = 53.581$, and $a_0 = 0.4065$ nm.

Circle-cross-section Au nanowires with diameter ranging from 3.25 to 6.50 nm are constructed from a large cubic fcc single crystal of gold using certain cylindrical cutoff radii centred at a cubic interstitial site, in which the crystallographic orientations are shown in Fig.1. In the Y and Z directions, the Au nanowire spans a finite number of unit cells, while in the X-direction an infinite wire is obtained by applying the periodic boundary condition. Three types of nanowires, i.e. [100], [110] and [111] nanowires, are considered in this paper.

We have performed molecular static simulations to relax fully these nanowires to a local minimum energy state using the conjugate gradient method. After the initial relaxation, the nanowires are under the equilibrium state without any external force so that the average stress over the cross-section is zero. The stress tensor in nanowire system can be defined as

$$\sigma_{\alpha\beta} = \frac{1}{V} \left\{ \sum_{i=1}^{N} m_i v_i^{\alpha} v_i^{\beta} + \sum_{i=1}^{N} \sum_{j>i}^{N} F_{ij}^{\alpha} R_{ij}^{\beta} \right\}, \tag{4}$$

where V and N are the volume and total atomic number of the system, m_i and v_i are the mass and velocity of the ith atom, F_{ij} and R_{ij} are the force and distance between atoms i and j. The first summation in Eq.(4) is zero at absolute zero temperature. α and β can be

arbitrary one of the X, Y and Z directions, but here both α and β are chosen to be X direction in which the elastic properties are mainly concerned.

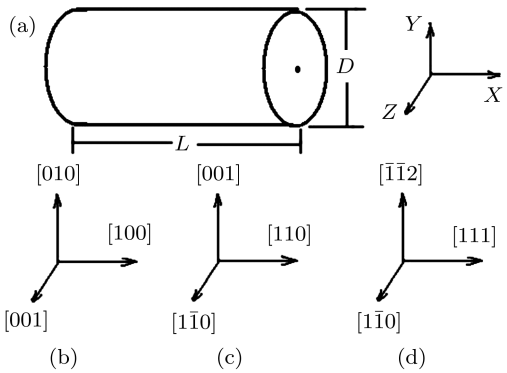


Fig.1. Schematic illustration of the simulation cell used to study the equilibrium characteristics of nanowires. The Z axis is the axial direction, and is subjected to periodic boundary conditions, while the surface is free. (b)–(d) illustrate the crystallographic directions of gold nanowires. D and L denote the diameter and length of the simulated cell, respectively.

This paper has simulated Au bulk and Au nanowires separately to study their elastic behaviour under the uniaxial tensile loading. After the initial fully relaxation, the nanowires are essentially stress free. A uniaxial tensile strain is applied along the X axis in the range from 0.0 to 1.0% with a -0.01% increment at each strain step. The periodic boundary conditions are applied in the X, Y and Z directions under uniaxial loading process. The conjugate gradient method is again employed to determine the energy minimum following each strain step. Some research have shown that the nanowires display a good linear elastic behaviour,[19,20] so the total stain of nanowires and bulk is 0.01 in order to ensure their deformation to be in linear elastic region.

3. Results and discussion

Firstly, we use molecular static approach to stimulate the elastic response of Au bulk under the uniaxial tensile loading. In the loading process, we calculate the normal stress in the system as a function of strain according to Eq.(4), and the stress-strain relations can be obtained in different directions. Figure 2 shows the elastic responses of Au bulk in the range of axial strain $0 \leq \varepsilon \leq 0.01$. For all three directions, the stress–strain relation is well linear below 1.0% strain. We adopt a linear function to fit the stress–strain points with the framework of the least square method, and acquire the Young's modulus of Au nanowire to be 72.2 GPa, 104.1 GPa and 157.1 GPa for [100], [110] and [111] direction, respectively.

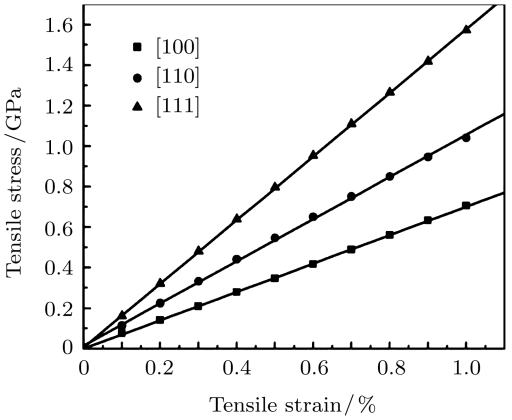


Fig.2. The elastic response of Au bulk for uniaxial strain applied along [001], [011] and [111] directions under tensile loading.

Similarly, the Young's modulus of Au nanowires may be obtained from their stress-strain curves. Figure 3 shows the dependence of the Young's modulus on diameter for [100], [110] and [111] nanowires. With the increasing of diameter, the Young's modulus of all three orientational nanowires increases and trends to that of bulk counterpart. For example, [100] nanowire's Young's modulus increases from 57.1 GPa to 66.2 GPa (below 72.2 GPa for bulk) while its diameter increases from 3.25 to 6.5 nm. This result should be attributed to the structural characteristics of nanowire. As we know, the elastic modulus is closely associated with the atomic binding intensity.

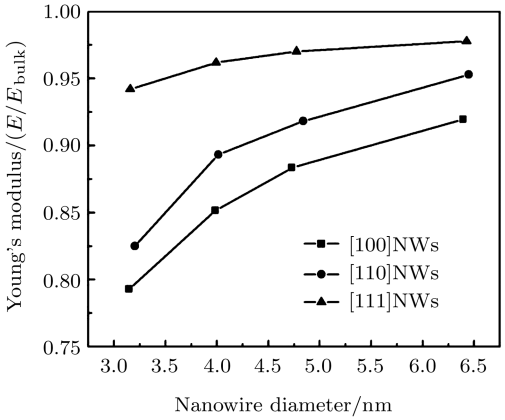


Fig.3. The Young's modulus as a function of diameter for [100], [110] and [111] nanowires.

With the decreasing of diameter, the nanowires are formed by a reduced number of atoms and the majority of them are located at the surface. The coordination number of surface atoms is far smaller than that of bulk atoms (i.e. 12), and the symmetrical degree of surface atoms is also much lower than that of bulk atoms. All above could weaken the bonding intensity between surface atoms, and further, in some sense, result in a low elastic modulus of nanowires.

In order to further investigate the elastic properties of nanowires, it is necessary to divide the nanowire into core and surface region. However, there is no absolute physical boundary between these two regions because it is a gradual process from centre layer to outmost layer for nanowire. For research convenience and simplification of the problem, we use the common neighbour analysis (CNA)[21] to determine whether or not an atom belongs to surface region. This analysis assigns four indices to each pair of atoms, which have common neighbours, and provides a description of the local environment of the pair. All bonded pairs in a fcc crystal are of type 1421, while a hcp crystal has equal numbers of type 1421 and 1422. We have calculated CNA indices in a number of atomic configurations extracted from molecular static calculations. Considering that pairs beside types of 1421 and 1422 cannot reveal some useful information for fcc metallic nanowire, we have classified all atoms into three categories. Atoms in a local fcc order are considered to be inside the nanowire; atoms in a local hcp order are classified as stacking faults. Atoms in all other local orders are considered to be part of surface. This analysis has been successfully used to analyse the structural evolution during the mechanical loading and melting process,[22,23] and proved to be an effective method.

We have calculated the surface volume of nanowires using the CNA methods, and illustrates the dependence of the surface volume to bulk ratio on the diameter for [100], [110] and [111] nanowires in Fig.4. As expected, this ratio increases with the decreasing of nanowire diameter, showing a strong size effect. The curves of [100] and [110] nanowires are almost overlapped, and lower than that of [111] nanowire. Since the bonding intensity between surface atoms is weaker than that of core, we may deduce from this figure that the Young's modulus of nanowires should increase with the decrease of the surface volume to bulk ratio when the diameter increases (see Fig.3).

If the surface thickness is considered to be a constant δ, in terms of theory of continuum media matter, the surface volume ratio can be expressed as the formulation

$$f(D) = 4\delta/D - 4\delta^2/D^2, \tag{5}$$

where D is the nanowire diameter. Due to the fact of a nanowire consisting of many discrete atoms, the true relation between surface volume ratio and diameter is somewhat deviated from this formulation. Approximately, we apply the following expression

$$f(d) = a/D - b/D^2 \tag{6}$$

to fit the discrete points in Fig.4, and show the fitted curves in this figure. We can roughly deduce from these fitted results that the surface thickness $\delta \approx a/4$, is about $0.7a_0$ for all three orientational nanowires (a_0 is the lattice constant of bulk). This is in general agreement with the prior simulations on bicrystal[24] if we consider that the thickness of bicrystal interface (i.e. $1.6a_0$) is about twice that of surface. These results also imply that surface region approximately consists of two layer atoms.

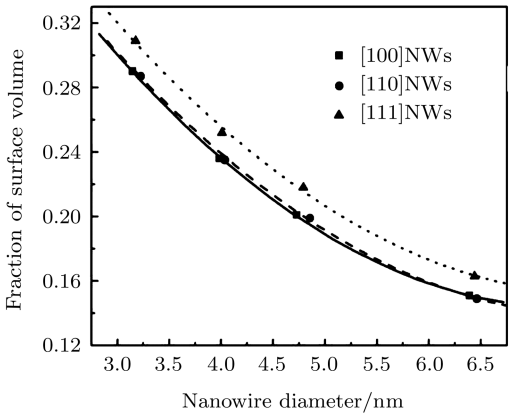


Fig.4. The surface volume to bulk ratio as a function of diameter for [100], [110] and [111] nanowires.

Further, we consider that the Young's modulus of nanowire is constituted of two parts: that of core and surface region, the following expression can be easily acquired

$$\begin{aligned} E &= E_s\left(\frac{A_s}{A}\right) + E_c\left(\frac{A - A_s}{A}\right) \\ &= E_s f_s + E_c(1 - f_s), \end{aligned} \tag{7}$$

here E and A are the Young's modulus and cross-section area of nanowire, the suffix c and s denote core and surface region, f_s is surface volume to bulk ratio. Considering that atoms in core region are in a local fcc structure, we think the Young's modulus of core to be equal to that of bulk.

According to the Eq.(7), we have extracted the Young's moduli of surface, and have illustrated them in Fig.5. It can be seen that the elastic modulus of surface region is much lower than that of single crystal, and increases slightly with the increasing of diameter. This result can be explained as follows: with the increasing of nanowire diameter, surface curvature and the number of unsaturated bond decrease, and the bonding intensity between surface atoms trends to higher, resulting in the increase of the elastic modulus in surface region.

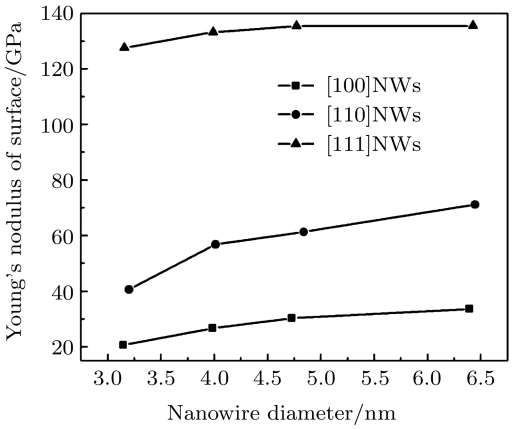


Fig.5. The dependence of Young's modulus of surface region on diameter for [100], [110] and [111] nanowires.

Generally, one-dimension nanomaterials have own preferred orientation during the growing process in experiments. Considering that the crystal should be most stabile when its energy is lowest, we may deduce that the crystallographic direction in which the nanowire presents the lowest potential energy state is the preferred orientation. Figure 6 shows the atomic average potential energy of nanowires with different diameters and crystallographic directions. Evidently, the potential energy of nanowires is higher than that of Au bulk (–3.826 eV for the calculated data and –3.81 eV for experimental data[25]). This is mainly owing to the surface characteristics of nanowire, i.e. the broken symmetry and low neighbour number of surface atoms, which make atomic potential energy in surface is much higher than that in bulk. The potential energy of [110] nanowire is lowest in all, whereas that of [111] nanowire is highest, and close to that of [100] nanowire. So we may deduce that the [110] direction is the preferential growth orientation, which is consistent with the experimental results.[26]

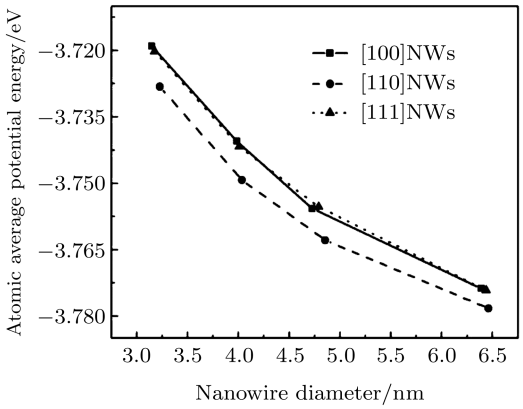


Fig.6. The diameter dependence of the atomic average potential energy for [100], [110] and [111] nanowires.

Further, we may calculate nanowires' surface energy by applying the following expression

$$\begin{aligned}\gamma_s &= \frac{(U - U_{\text{bulk}})\, N}{S} \\ &= \frac{(U - U_{\text{bulk}})\, N}{\pi D L},\end{aligned} \tag{8}$$

where U and U_{bulk} are the atomic average potential of nanowire and of single crystal, S is surface area of nanowire, D and L are the diameter and length of nanowire.

Figure 7 shows the surface energy of nanowire calculated from Eq.(8). It can be seen that surface energy of [110] nanowire is the lowest of all three orientational nanowires. For example, the surface energy of nanowire with 4nm diameter is 835 mJ/m^2 for [100] direction, 757 mJ/m^2 for [110] direction and 843 mJ/m^2 for [111] direction, respectively. Obviously, all calculated surface energy are lower than the experimental value (1506 mJ/m^2 for Au bulk,[27]) the resulting variations are mainly resulted from our computational models and applied external conditions. First, the simulated surface energy under absolute zero temperature is generally lower than that under room temperature. Secondly, our adopted potential models usually lead to a low surface energy calculated from atomistic simulations. Thirdly but importantly, many experiments are usually carried at room temperature to acquire the surface energy of Au bulk (or coarse-grained counterpart), whose surface is essentially constituted of many different facets. The computational surface energy decreases slightly with the increasing of nanowire diameter. This could be owing to decreasing of surface curvature and occurrence of more order structure in surface region when the diameter is increased, which deduce a resultant reduction in the potential energy and the surface energy.

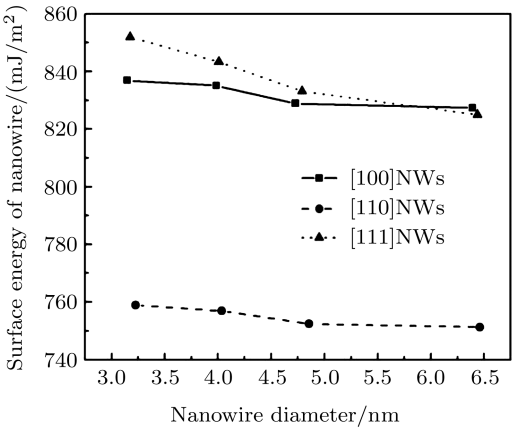


Fig.7. The surface energy as functions of diameter for three orientational nanowires.

4. Conclusions

In summary, we have employed molecular static approaches with the quantum corrected Sutten–Chen type many-body force field to investigate the elastic properties and the preferential growth orientation of Au nanowires with [100], [110] and [111] crystallographic orientations. The results show that for all three orientational nanowires, the Young's modulus increases with the increasing of diameter, and presents highest for [111] nanowire and lowest for [100] nanowire. In order to explore the elastic characteristics of surface, we have used the common neighbour analysis to divide the nanowire into two regions, *i.e.* surface and core regions, and deduce that surface region approximately consists of two layer atoms. Further, we extract the Young's modulus of surface in terms of theory of continuum media matter, and the calculations show that it increases slightly with the increasing of diameter. We also study the energy characteristics of nanowire, and the results show that both the potential and surface energy of [110] nanowire is the lowest of all three direction nanowires, which helps to explain why Au nanowires possess a [110] preferred orientation during the experimental growth proceeds.

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