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Size-dependent multilayer relaxation of nanowires and additional effect of surface stresses

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Abstract

A theoretical investigation was carried out on multilayer relaxation, surface energy and surface stress in [001] oriented rectangular f.c.c metal nanowires using the modified embedded atom method. Surprisingly, the multilayer relaxation behavior depends on the wire sizes in absolutely distinct trends for inward-relaxation metals Ag, Cu, and for outward-relaxation metals Ir and Ni. Specifically, the outmost interlayer relaxation $|\Delta d_{12}|$ increases with decreasing cross-section areas for Ag, Cu nanowires, while it decreases for Ir, Ni nanowires. This is due to the additional effect of surface stress, which, with the surface energy, increases with decreasing wire width monotonically.

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1. Introduction

Metal nanowires have been attracting more and more attention because of their singular structures, excellent properties and potential applications as general building blocks for logic and memory circuits, structural reinforcement in composite materials, and as sensors to detect airborne biological and chemical toxins [1,2]. On the whole, the fabrication approaches of nanometer-scale materials can be grouped into two classes: bottom–up [3–9] and top–down [10–14]. In the former case, nano-elements are usually deposited by utilizing certain physical or chemical processes with the aid of a template, while the latter case involves the fabrication of nano-components from bulk materials by thinning through optical-beam, electron-beam, ion-beam, or scanning-probe lithography. Compared with the "bottom–up" approaches, the "top–down" approaches possess great flexibility and can be used to prepare nano-elements of nearly any shape. During the top–down preparation process of nanowires, new surfaces are created, where the atomic coordination is reduced considerably. The neighbor atoms outside wires vanish, and thus asymmetrical Coulomb electrostatic forces are applied to the electrons near the surfaces. In such a case, the electrons must redistribute in three-dimensional space to smooth the differences of electron density, which has been addressed in many research works [15–17]. In return, the electron redistribution should drive the atomic cores to adjust their positions. One of the simplest processes is displacement only perpendicular to surfaces, so-called interlayer relaxation.

For semi-infinite crystals, many investigations have been carried out on multilayer relaxation through advanced experimental techniques, such as low energy electron diffraction (LEED) [18–21], low and medium energy ion scattering (LEIS, MEIS) [22,23], X-ray diffraction (XRD) [24], and so on. At the same time a great deal of theoretical work has also been performed on this issue using various methods from the semi-empirical embedded atom method (EAM) [25–27], tight-binding potentials (TB) [28,29], to *ab intio* density functional theory (DFT) [30–32]. Both experimental observations and theoretical analysis showed that the multilayer relaxation takes place mainly in the topmost six atomic layers, and damps from the surface into the bulk with an oscillatory behavior.

Conceivably, as the sizes of materials are comparative to the dimension scale of about several atomic layers, most of

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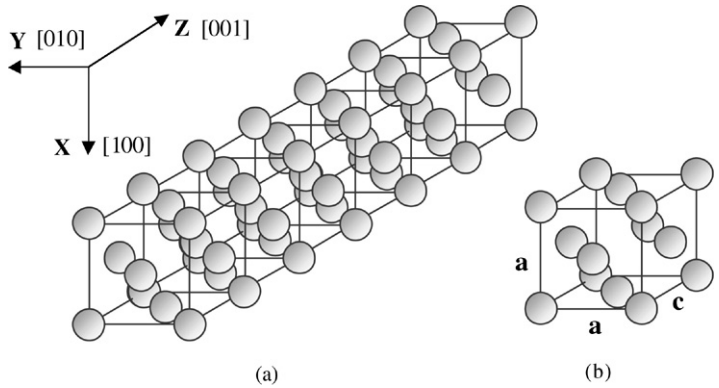

Fig. 1. An external view of a [001] oriented rectangular 3 × 3 f.c.c nanowire involved in this work (a), and the primitive cell of the nanowire (b).

the atoms can "feel" the existence of surfaces. In such a case, the multilayer relaxation may extend throughout the whole material, and should strongly depend on their sizes. Taking [001] oriented rectangular Ag, Cu, Ir and Ni nanowires as examples, this is investigated using the modified embedded atom method (MEAM) [33,34] in the present work.

2. Computational details

On the whole, there are two kinds of method which can be used to predict the structures and properties of materials: first principles and atomic potential. Although the former needs no external parameters and thus is extremely accurate, it is limited by present computational power, and can only be used to deal with systems of less than 100 atoms [35]. But the supercell of a 11 × 11 nanowire (in each transverse direction, there are 11 atom layers) already has 121 atoms, and, moreover, the larger the wire width, the more the atoms are included in a supercell. Therefore, a systematic investigation on the nanowires cannot be performed by first-principle methods. To overcome this difficulty, we used here a semi-empirical atomic-scale potential, the modified embedded atom method (MEAM). The MEAM was developed from the original EAM [36, 37] by including the angular dependence of atomic electron density and is now becoming a popular approach which is not only used to investigate the structures and properties of perfect bulk crystals [36–40], but has also tried to predict abnormal behaviors in nano-structured materials [41–45] and low-coordinated surfaces [46–49], especially for fcc metals. In MEAM, the total energy of a unary system is approximated as

$$E = \sum_i \left[F(\overline{\rho}_i) + \frac{1}{2} \sum_{j(\neq i)} \phi(R_{ij}) \right], \tag{1}$$

where $\overline{\rho}_i$ is the background electron density at site i, $\phi(R_{ij})$ is the pair interaction between atoms i and j separated by a distance R_{ij}. F is the embedding function, and is given as follows:

$$F(\overline{\rho}) = AE_c(\overline{\rho}/\overline{\rho}^0)\ln(\overline{\rho}/\overline{\rho}^0), \tag{2}$$

in which A is an adjustable parameter, E_c is the sublimation energy, and $\overline{\rho}^0$ is the background electron density in a reference structure, where individual atoms are on the exact lattice sites without deviation. Generally, the equilibrium structure is taken as the reference structure for elements. The background electron density $\overline{\rho}_i$ is composed of a spherically symmetric partial electron density $\rho_i^{(0)}$ and three angular dependent contributions $\rho_i^{(1)}$, $\rho_i^{(2)}$, and $\rho_i^{(3)}$. For their exact expressions and relevant parameters, the readers can see Refs. [33] and [34].

In top–down fabrication processes, it is convenient to prepare [001] oriented rectangular f.c.c metal nanowires with (010) and (100) side surfaces from the bulk. As an example, Fig. 1(a) shows the model of a nanowire with cross-section of 3 × 3 atom layers. The wire length along the longitudinal direction Z is assumed as infinity to avoid end effects. Wider wires can be simulated by adding more atomic layers along two transverse directions, X and Y, simultaneously. All the atomic layers will be completely relaxed using a simple conjugate gradient technique to minimize the energy of the nanowires. During the whole relaxation process, the tetragonal symmetry of the wires is kept, and a periodic boundary condition is applied in the Z direction. The lattice parameters along the Z direction are invariable, only the lattices along the X and Y directions contract or dilate to arrive at a minimum energy.

After the multilayer relaxation, we also calculate the surface energy and surface stress in the final atom configurations. The surface energy E_{surf} is the reversible work per unit area needed to create a new surface and can be calculated as follows:

$$E_{\text{surf}} = \frac{\sum_i (E_i - E_0)}{A_{\text{surf}}} = \frac{\sum_i (E_i - E_0)}{4 \times W \times L}, \tag{3}$$

where E_i is the energy of atom i, E_0 is the cohesive energy per atom in a bulk crystal. A_{surf}, W and L are the total surface area, width and length of nanowires respectively. The sum is done over all atoms. Taking into account the crystal periodicity along the longitudinal direction, a face-centered-tetragonal computational cell (see Fig. 1(b)) is enough for our purposes. Different from the surface energy, the surface stress is the reversible work per unit area needed to elastically stretch a pre-existing surface [50], and must be a tensor. In other words, the surface stress tensor $\tau_{\alpha\beta}$ can be defined as the strain derivative of the surface energy. Assuming a homogenous strain $\varepsilon_{\alpha\beta}$ ($\alpha, \beta \in (x, y)$) is applied within surface planes,

$$\tau_{\alpha\beta} = A_{\text{surf}}^{-1} \cdot \partial(E_{\text{surf}} \cdot A_{\text{surf}})/\partial\varepsilon_{\alpha\beta}. \tag{4}$$