Surface-stress-induced phase transformation in metal nanowires

JIANKUAI DIAO*, KEN GALL AND MARTIN L. DUNN
Department of Mechanical Engineering, University of Colorado, Boulder, Colorado 80309, USA
*e-mail: diao@colorado.edu

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Several researchers1–8 have demonstrated, through experiments and analysis, that the structure and properties of nanometre-scale materials can be quite different to those of bulk materials due to the effect of surfaces. Here we use atomistic simulations to study a surface-stress-induced phase transformation in gold nanowires. The emergence of the transformation is controlled by wire size, initial orientation, boundary conditions, temperature and initial cross-sectional shape. For a <100> initial crystal orientation and wire cross-sectional area below 4 nm², surface stresses alone cause gold nanowires to transform from a face-centred-cubic structure to a body-centred-tetragonal structure. The transformation occurs roughly when the compressive stress caused by tensile surface-stress components in the length direction exceeds the compressive stress–strain in the core of the wire, ultimately inducing a phase transformation from an f.c.c. structure into a body-centered-tetragonal (b.c.t.) structure below a cross-sectional area near 4 nm². Wires with initial <111> and <110> orientations did not undergo the f.c.c.–b.c.t. phase transformation. The structural transformation has not been discovered in previous studies on nanowires9–13 because of key differences in the initial orientations, initial cross-sectional shape, and boundary conditions of the wires. In fact, our simulations predict the reorientation and reshaping of <100> wires into <110> wires with [111] surfaces, in line with experimental observation3 (see Supplementary Information).

We investigate the energetics and structure of Au nanowires with an initial <100> orientation and a square cross-section. The tensile surface-stress components in the length direction cause a significant compressive stress–strain in the core of the wire, ultimately inducing a phase transformation from an f.c.c. structure into a body-centered-tetragonal (b.c.t.) structure below a cross-sectional area near 4 nm². Wires with initial <111> and <110> orientations did not undergo the f.c.c.–b.c.t. phase transformation. The structural transformation has not been discovered in previous studies on nanowires9–13 because of key differences in the initial orientations, initial cross-sectional shape, and boundary conditions of the wires. In fact, our simulations predict the reorientation and reshaping of <100> wires into <110> wires with [111] surfaces, in line with experimental observation3 (see Supplementary Information).

We used the modified embedded atom method (MEAM) with Au potential developed previously14,15. Au [100] nanowires with a square cross-section and surface orientations of [100], [010] and [001] were created with initial atomic positions corresponding to the bulk f.c.c. crystal. The original length of the wires was 32 nm and the cross-sectional area was varied. The wires were then relaxed to a minimum energy state in a molecular static framework at 0 K using the conjugate gradient method. Free boundary conditions were used in all directions.

Owing to the tensile surface-stress components in the length direction, the wires contract on relaxation. For wires with an initial cross-sectional area larger than 1.83 nm × 1.83 nm, the contraction is less than 4% and is realized by nonlinear elastic compression of the wire. However, when the initial cross-sectional area is equal to or less than 1.83 nm × 1.83 nm, the contraction in the length direction exceeds 30%. Figure 1a shows the unrelaxed and relaxed configurations of the 1.83 nm × 1.83 nm wire with the atoms coloured by a centrosymmetry parameter of, a measure of the degree to which a given atom is locally a centre of inversion symmetry. This parameter is zero for a perfect f.c.c. crystal and becomes non-zero at structural defects including crystal surfaces. Figure 1b,c,d shows the cross-sections at the centre region of the unrelaxed and relaxed 1.83 nm × 1.83 nm nanowire, observed from the x, y and z directions, respectively. Only two adjacent lattice planes of atoms are shown as the lattice planes repeat in an ABAB stacking sequence.
In Fig. 1b,c,d, the atoms in A and B planes are shown in different colours, and are not coloured by the centrosymmetry parameter.

Crystallographic arguments show that a phase transformation occurs from the original f.c.c. structure to a b.c.t. structure for wires with initial cross-sectional area equal to or less than 1.83 nm × 1.83 nm.

Consider a unit cell of the unrelaxed 1.83 nm × 1.83 nm wire, which is an f.c.c. cell with a lattice constant of 4.07 Å. After relaxation, owing to the contraction in the x direction, the length of the cell in the x direction becomes 2.824 Å. Meanwhile the wire expands in the y and z directions on relaxation and the length of the cell in those directions become 4.758 Å. The contraction and expansions change the structure of the wire from the original f.c.c. to b.c.t. with lattice parameters of a = 4.758/√2 Å and c = 2.824 Å. We should mention that the values of the lattice constants are averaged values over all unit cells except those at ends of the wire. Owing to the phase transformation, the side surfaces of the relaxed wire are all hexagonally close-packed and contracted 1.9% in the x direction and 4.5% in the y and z directions with respect to an f.c.c. Au [111] plane lattice.

We also conducted molecular dynamic simulations at 100 K on the 1.83 nm × 1.83 nm wire to study the dynamics of the phase transformation with free boundary conditions identical to those in the static simulations. Figure 2 shows the dynamic progression of the phase transformation in the 1.83 nm × 1.83 nm wire. The phase transformation nucleates from the ends of the wire, and propagates toward the centre at an average speed of 347 m s⁻¹. This propagation speed is about one order of magnitude slower than the longitudinal sound-wave speed in gold. The phase transformation front represents a coordinated shift of the atoms from the f.c.c. lattice to the b.c.t. lattice. We verified the stability of the b.c.t. nanowire by simulated annealing. The temperature was raised from 100 K to 600 K gradually, kept at 600 K for 1 ns (10⁶ timesteps) and then lowered to 100 K gradually. The b.c.t. wire kept its structure during the entire annealing process. The molecular dynamic simulation is of particular interest, as it demonstrates how the local minimum energy state predicted by the static simulation is achieved by the nucleation and propagation of a phase transformation throughout the wire. As is the case with many

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Figure 1 The phase transformation in the 1.83 nm × 1.83 nm <100> wire. a. Unrelaxed and relaxed configurations of the wire. Atoms are coloured according to the centrosymmetry parameter. b, c, d. Cross-sections at the center regions of the unrelaxed and relaxed wires, observed from x, y and z directions respectively, only two adjacent lattice planes of atoms are shown, and atoms in different lattice planes are shown in different colours. In c and d only partial regions of the wires are shown in the x direction.
solid-state phase transformations, the nucleation is heterogeneous, occurring at the ends of the wire in a region with elevated non-uniform stress. The heterogeneous nature of the transformation implies that it will be strongly dependent on boundary conditions and local structural features.

The surface stress can be viewed as the driving force for the phase transformation. A simplified continuum model of a nanowire, considering only the surface-stress components in the length direction, can be constructed by subjecting a bulk wire to an externally applied force to create a compressive stress. Given the stress required to induce the phase change in the bulk wire, and the surface-stress magnitude, the simplified model can be used to estimate the critical nanowire size that will cause the transformation. To estimate this critical nanowire size, we performed uniaxial compression-loading in the [100] direction of bulk gold under force control. Periodic boundary conditions were used in the [100], [010] and [001] directions to emulate bulk gold. Force was applied in the [100] direction and the periodic lengths in all the three directions were allowed to adjust to the applied load.

Figure 3 shows the compressive stress–strain curve for bulk gold. As the compression load is increased, the deformation initially follows the path (1), at a critical stress of 1.6 GPa, the deformation jumps from path (1) to path (2), and at a critical stress of 3.7 GPa, the deformation jumps from path (2) to path (3). Throughout the entire loading process, the tetragonal symmetry is maintained, that is, the deformation is along the Bain path. Two distinct structures were observed in paths (2) and (3). We unloaded the force from the paths (2) and (3) to investigate the resulting stress-free structures. They are both b.c.t., one with \( a = 4.260/\sqrt{2} = 3.012 \) Å and \( c = 3.595 \) Å, the other with \( a = 4.813/\sqrt{2} = 3.404 \) Å and \( c = 2.856 \) Å. We will refer to those two new structures as b.c.t.1 and b.c.t.2, respectively, in the following text.

The average lattice constants of the transformed nanowires in Figs 1a and 2 are about 1% smaller in both \( a \) and \( c \) than those of the bulk b.c.t.2 structure due to the tensile surface stresses on the transformed wires. Consequently, the static and dynamic simulations presented in Figs 1 and 2 only show evidence of the b.c.t.2 structure. We explain this apparent discrepancy in the following text.

Using a method similar to that of Streitz et al., we calculated the surface-stress components for the unstrained f.c.c., b.c.t.1 and b.c.t.2 structures for various crystallographic planes and orientations (Table 1). The tensile surface-stress components in the length direction on the four side surfaces of a nanowire induce a compressive stress in the nanowire. At equilibrium, the magnitude of the induced compressive stress can be estimated as \( \sigma = 4f/\Lambda \), where \( f \) is the surface-stress component, \( l \) is the width of a nanowire (the length over which the surface-stress component acts), and \( \Lambda \) is the cross-sectional area. In a relaxed nanowire, the tensile surface-stress component and the induced compressive stress balance each other and the average stress is zero over the cross-sectional area. When the induced compressive stress in a...
However, a slightly smaller critical size of 1.83 nm required for the phase change from f.c.c. to b.c.t.1 in bulk gold. The tensile surface-stress components in transverse directions hinder the phase transformation, lowering the actual wire size necessary for the transformation.

We have shown that the surface stresses of the f.c.c. 1.83 nm x 1.83 nm wire are large enough to induce the wire to transform from f.c.c. to b.c.t.1. However, in both the static and dynamic simulations, the wire ultimately transforms to the b.c.t.2 structure. The b.c.t.1 wire is not observed in the simulations because its surface-stress component in the length direction is considerably higher than that of the f.c.c. wire, 2.85 J m⁻² versus 1.03 J m⁻², respectively (Table 1). The magnitude of the compressive stress induced by the surface-stress component in the length direction of the b.c.t.1 wire is 5.95 GPa. This stress is much larger than the critical stress of 3.72 GPa required to induce phase transformation from b.c.t.1 to b.c.t.2 in bulk gold. Consequently, the surface stresses induce two successive phase transformations in the 1.83 nm x 1.83 nm wire. We should mention that in dynamic simulations at lower temperature (10 K) we did observe b.c.t.1 structure, the f.c.c. wire transforms first to the b.c.t.1 wire, and then the b.c.t.1 wire transforms to the b.c.t.2 wire.

We have examined the energetics of the phase transformation using static simulations. The calculated cohesive energies for bulk f.c.c., b.c.t.1 and b.c.t.2 gold are listed in Table 1 along with the respective surface energies. We see that bulk b.c.t.1 and b.c.t.2 gold have higher energies per atom than the bulk f.c.c. gold, but lower surface energies for the specific surfaces of the wire. The total energies of f.c.c. wires will crossover those of the b.c.t.1 and b.c.t.2 wires as the wire size decreases (The total energy of the b.c.t.2 wire is always lower than that of the b.c.t.1 wire). We estimated that when the cross-sectional area of an f.c.c. wire is less than 30.1 nm x 30.1 nm, the corresponding b.c.t.2 wire has the lowest total energy. However, in our static simulations we do not predict the transformation to b.c.t.2 structure until a much smaller wire size. The phase transformation will not occur just because the total energy of the b.c.t.2 wire is lower than that of the corresponding f.c.c. wire. Energy barriers exist between the f.c.c. and the corresponding b.c.t.2 wires. For wires with cross-sectional area equal to and less than 1.83 nm x 1.83 nm, the surface stresses alone can overcome the energy barriers, as seen in the static simulation. For wires with cross-sectional area in between 1.83 nm x 1.83 nm and 30.1 nm x 30.1 nm, the surface stresses alone cannot overcome the energy barriers. The addition of thermal vibrations may help to overcome energy barriers. For example, we observed phase transformation in the dynamic simulation of a 2.65 nm x 2.65 nm wire at an elevated temperature of 300 K.

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Competing financial interests

The authors declare that they have no competing financial interests.