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# Effects of surface atomistic modification on mechanical properties of gold nanowires

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ABSTRACT

Modulation of the physical and mechanical properties of nanowires is a challenging issue for their technological applications. In this paper, we investigate the effects of surface modification on the mechanical properties of gold nanowires by performing molecular dynamics simulations. It is found that by modifying a small density of silver atoms to the surface of a gold nanowire, the residual surface stress state can be altered, rendering a great improvement of its plastic yield strength. This finding is in good agreement with experimental measurements. The underlying physical mechanisms are analyzed by a core–shell nanowire model. The results are helpful for the design and optimization of advanced nanomaterial with superior mechanical properties.



## 1. Introduction

Nanomaterials hold great promise for potential applications in a variety of fields, e.g., fuel cells, biomedical engineering, medicine, and ultrahigh-strength materials [1–3]. The physical properties of nanomaterials are often critically dependent on the surface effects originating from the symmetry breaking of atomistic structures close to surfaces [4–9]. By manipulating the surface parameters related to a few atomic layers near the surface, nanomaterials can be designed to possess novel properties. For example, Kim et al. [10] investigated the effect of surface modification of carbon nanotubes on the mechanical properties of carbon nanotube/epoxy composites. They found that surface modification can render more homogeneous dispersion of carbon nanotubes and achieve stronger adhesion between the carbon nanotubes and the matrix. Jin and Weissmüller [11] accomplished a repeatable and fast change in the yield strength, flow stress, and ductility of nanoporous gold (Au) by surface polarization. Besides, Biener et al. [12] demonstrated that atomic layer deposition can stabilize the morphology of nanoporous metals up to an ultrahigh temperature and improve their tensile strength. Using the concept of surface elasticity, Duan et al. [13] predicted that nanochannel-array materials can be made stiffer by surface modification. Hodge et al. [14] performed depth-sensing nanoindentation tests to Ag-coated nanoporous Au samples, and illuminated the effects of residual silver (Ag) atoms on the elastic properties of nanoporous Au.

In-depth investigations of surface modification effects on the mechanical properties of nanomaterials are of great interest for their fabrication and performance improvement. However, the atomic-level mechanisms by which surface modification affects the mechanical properties of nanomaterials remain elusive. In this paper, we performed molecular dynamics (MD) simulations to investigate the mechanical behaviors of nanowires with surface modification by Ag atoms. The mechanisms underlying the surface effects are revealed via a core–shell nanowire model.

## 2. Methods

Due to its huge surface-to-volume ratio, nanoporous Au is an ideal candidate for studying the effects of surface modification on mechanical properties [14–17]. Nanoporous Au is commonly fabricated by dealloying Au/Ag alloys [18–20], and it can essentially be regarded as a three-dimensional network consisting of a large number of connected nanowires [21,22]. However, it is difficult to directly perform full-atomistic simulations for nanoporous Au. Therefore, we chose Au nanowires coated with Ag atoms in our model system to study the effects of surface modification and the underpinning atomistic mechanisms. Typical ligament radius of nanoporous ranges from 2 nm to 50 nm [18,23], and most ligaments have irregular cross sections and nonuniform dimensions

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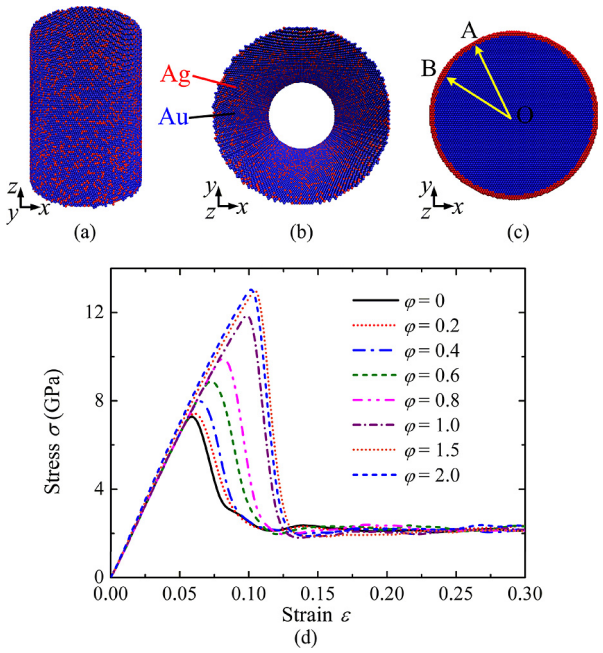


**Fig. 1.** Simulation model and mechanical properties of surface modified nanowires. (a) Side view and (b) top view of an Au nanowire with surface modification. For clear illustration, only the Au atoms (blue) on the surface and the Ag atoms (red) are shown, while the Au atoms in the core of nanowire are hidden. (c) Configuration of an Au nanowire with SSF $\varphi = 2.0$. (d) Stress–strain curves of Au nanowire samples, where the SSFs are 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, and 2.0, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

along their length directions. In this study, the ligament is approximately regarded as a cylindrical Au nanowire.

Figs. 1(a) and 1(b) show, respectively, the lateral and the vertical views of the model, i.e., a surface modified cylindrical Au nanowire of radius $r = 10$ nm and length $l = 25$ nm. The Ag surface modification to Au nanowire is performed by the following two steps. Firstly, the surface atoms of a single-crystalline face-centered cubic (FCC) Au nanowire are identified by using the common neighbor analysis (CNA) method [24]. In this example, the number of surface Au atoms is 24 955, about 5.46% of the total 457 275 atoms. Secondly, a certain fraction of Au atoms, with a random distribution on the nanowire surface, are replaced by Ag atoms. For clear illustration, only the Au atoms (blue) on the surface and the Ag atoms (red) are shown in Figs. 1(a) and 1(b), the Au atoms in the interior of the nanowire are not displayed. The surface silver fraction (SSF) is defined as $\varphi = N_{\mathrm{Ag}}/N_{\mathrm{surface}}$, where $N_{\mathrm{Ag}}$ and $N_{\mathrm{surface}}$ are the number of Ag atoms and the total number of surface atoms, respectively. To investigate the dependence of mechanical properties on SSF, six nanowires with $\varphi = 0$, 0.2, 0.4, 0.6, 0.8, and 1.0 are simulated.

The molecular dynamics simulations are performed by using LAMMPS [25]. All nanowires have $z = \langle 111 \rangle$ in the longitudinal orientation, and $x = \langle 11\bar{2} \rangle$ and $y = \langle \bar{1}10 \rangle$ in the other two directions. Periodic boundary conditions are imposed in the axial direction, i.e., $z$ direction, while the lateral surfaces are traction-free. The embedded atom method (EAM) potentials [26] are utilized to describe the interatomic interactions for Au, Ag and Au–Ag, and the time step is set as 1 fs. Before loading, each nanowire is relaxed for 20 ps to reach its minimum energy state by using the conjugate gradient method and then to reach thermodynamic equilibrium through a Nosé–Hoover thermostat. Simulations are run at the temperatures of 1 K and 300 K, and similar trends are observed in the two cases. To filter out the noise resulting from thermal effects, only the simulation results at 1 K are presented in the following. After relaxation, uniaxial tension is applied by stretching the simulation box along the axial direction. In each loading step, a uniform strain increment of 0.1% is prescribed, and then the nanowire is relaxed for 1 ps. Atomic stresses are calculated using the Virial theorem [27], and the Virial stress is averaged over the last 50 fs of the relaxation period at each loading step. Visualization is carried out by using the Visual Molecular Dynamics (VMD) tool [28].

## 3. Results and discussions

### 3.1. Mechanical properties of surface modified nanowires

The uniaxial tensile stress–strain curves of the six nanowire samples are shown in Fig. 1(d). In the initial deformation stage, the stress increases linearly with the strain until the plastic yield stress $\sigma_{\mathrm{p}}$ is reached. Young's modulus calculated from the stress–strain curve is about 132 GPa for the pure Au nanowire and the results for the elastic moduli of the other five surface modified nanowires display little difference. Following the elastic regime of deformation, the stress–strain curves of the nanowires show a precipitous drop, implying the occurrence of plastic flow. The yield stresses of the modified nanowires with the SSF $\varphi = 0.2$, 0.4, 0.6, 0.8, and 1.0 are 7.56, 8.09, 8.98, 10.03, and 12.17 GPa, respectively, while the yield stress of the pure Au nanowire is 7.42 GPa. Clearly, the plastic yield stress increases significantly with an increase in the SSF though the ratio between the Ag atoms and the total atom numbers in the nanowire is still very low. For example, the plastic yield stress $\sigma_{\mathrm{p}}$ of the Au nanowire with $\varphi = 1.0$ is about 64% higher than that of the pure Au nanowire though its surface Ag atom number is only 5.46% of the total atom number. This results is in reasonable agreement with recent experimental measurements [12,14]. Therefore, appropriate surface modification can greatly improve the strength of nanowires.

In experiments, Ag atoms may substitute not only a certain part of the Au atoms in the first surface layer but also those at the second, third or even deeper layers, rendering a gradient distribution of Ag atoms [12,14]. This case is also simulated in this work. As displayed in Fig. 1(c), all atoms in the first to the third surface layers of the Au nanowire are replaced by Ag atoms, corresponding to a SSF of $\varphi = 2.0$. Due to the difference of crystal orientations, the modified Ag atoms in some orientations (e.g., OA direction in Fig. 1(c)) are located in the first and the second layers while those in some other orientations (e.g., OB direction in Fig. 1(c)) are in the first, the second, and the third layers. Similarly, the value of SSF $\varphi = 1.5$ corresponds to the case when the surface atoms in the first and the second layers are replaced by Ag atoms. The uniaxial tensile stress–strain curves of the samples with $\varphi = 1.5$ and $\varphi = 2.0$ are also plotted in Fig. 1(d). It is found that the plastic yield stress $\sigma_{\mathrm{p}}$ of the Au nanowire with $\varphi = 1.5$ is 13.29 GPa, about 9.2% higher than that with $\varphi = 1.0$. However, the Au nanowire with $\varphi = 2.0$ has $\sigma_{\mathrm{p}} = 13.31$ GPa, which is almost the same as that with $\varphi = 1.5$. This evidences that the change in $\sigma_{\mathrm{p}}$ results mainly from surface effects.

To reveal the atomistic mechanisms underpinning the observed deformation behavior, we take the nanowire with $\varphi = 0.2$ as an example to investigate the microstructural evolution during plastic deformation. Fig. 2(a) captures the atomic configuration of the nanowire at an initial plastic deformation state under the strain $\varepsilon = 0.058$. The defects are identified by the CNA methods. The Au atoms are painted in different colors according to their atomic structures: green for hexagonal-close-packed (hcp) atoms and blue for non-12-coordinated atoms. The Au atoms in the perfect face-centered-cubic (fcc) structure are not shown in order to visualize the interior atomistic defects. The Ag atoms are painted in red color. It is observed that a few different slip systems have