Anisotropic and temperature effects on mechanical properties of copper nanowires under tensile loading

Yajun Gao, Hongbo Wang, Jianwei Zhao, Changqing Sun, Fengyin Wang

**1. Introduction**

In the past decade, the metallic nanowires (NWs) have been the focus of intense research principally due to their unusual mechanical, electrical, catalysis and thermal properties [1–6]. These properties of NWs result from their finite size, low-coordinate of surface atoms and thus help them find application in many different areas such as active components of circuits [7], sensors [8,9] and resonators [10] in nano-electromechanical systems (NEMSs). For this reason, well understanding the mechanical properties in elastic and plastic deformation is essential.

A great deal of experimental and theoretical effort has been made to elucidate the structural and mechanical properties. The invention and refinement of experimental techniques, such as mechanically controllable break junctions (MCBJs) [11–14], high-resolution transmission electron microscopy (HRTEM) [15–17], atomic force microscopy (AFM) [18,19] and scanning tunneling microscopy (STM) [20,21], have made it possible to evaluate the properties of NWs. In elongation experiments, metal NWs show highly distinct plastic deformation and fracture modes that strongly depend on crystallographic orientation [22–25]. The (1 1 0) oriented NWs form a stable nanobridge during necking under tensile loading. In contrast, (1 0 0) and (1 1 1) oriented NWs produce short and disordered necked regions. Compute simulation technique, especially molecular dynamics (MDs) simulation, is an alternative approach to evaluate the properties of the NWs and explain the fundamental mechanisms in the process of the mechanical deformation. The failure modes of face-centered cubic NWs with the (1 0 0) orientation, related to size and strain rate, have been extensively studied [26–33]. For instance, Diao et al. [27,28] studied the effect of surface stress driven reorientation using embedded-atom method. Wen et al. [32,34] employed the quantum corrected Sutten-Chen type many body potentials to study strain rate induced amorphization in Ni NWs. In addition, Koh and Lee [30] employed the Finnis–Sinclair potentials to study size and strain rate effects in Pt and Au NWs.

Besides, we lately became aware of the mechanical properties of NWs also dependent on thermal energy [35–37]. A study to find the temperature effects on mechanical properties of Cu NWs under tension has not been performed before. In this research, the anisotropic and temperature effects were analyzed with different crystallographic orientations to investigate mechanical properties of Cu NWs. The stress–strain responses were followed by a particular discussion on yield mechanism of NWs from the standpoint of dislocation moving. Generally, the study on the incipient plastic deformation will be helpful to further understanding of the mechanical properties of nanomaterials. In addition, the Young's modulus decreased linearly with the increase of temperature. The crystal structure is less stable at elevated temperatures.

**2. Methodology**

Considering that most of NW models created from bulk fcc crystal possessed square cross-sections [27–33,38], three types of Cu NWs with square cross-sections are constructed for analogous simulation, i.e., (1 0 0), (1 1 0) and (1 1 1) oriented Cu NWs,
EAM potential functions as following [50]:

\[
E = \frac{1}{2} \sum_y V(r_y) + \sum_i F(\rho_i),
\]

(1)

\[
\rho_i = \sum_{ij} \phi(r_{ij})
\]

(2)

where \(E\) is the total internal energy of the system, \(V\) is the pair potential between atoms \(i\) and \(j\), and \(r_{ij}\) is the distance between them, \(F(\rho_i)\) is the energy to embed atom \(i\) in an electron density \(\rho_i\), \(\phi(r_{ij})\) is the electron density at atom \(i\) due to atom \(j\) as a function of the distance \(r_{ij}\). All the presented MD simulations and visualization process were performed with a self-developed code, NanoMD [42], which uses a combined Verlet leapfrog and cell-linked list algorithm. The reliability of algorithms has been validated not only by a number of theoretical simulations [43–48], but also by the comparison to the experimental measurements [49].

The stress within the NWs is computed by the virial scheme, and the overall stress is taken as the average of all atomistic stresses. Note that we are only concerned with the stress in the \(z\) direction, and the corresponding atomic stress is expressed in terms of EAM potential functions as following [50]:

\[
\sigma_z = \frac{1}{\Omega z} \left\{ -m_z v_z^2 + \frac{1}{2} \sum_{j \neq z} \left[ \frac{\partial F}{\partial \rho_z} \frac{\partial F}{\partial \rho_j} \right] \frac{r_{zj}^2}{r_{zj}} \right\}
\]

(3)

where \(\sigma_z\) is the \(z\) component of the atomic stress tensor of atom \(z\), \(\Omega z\) is its volume, \(m_z\) is the mass, and \(v_z^2\) is the velocity component in the \(j\) direction of atom \(z\). \(F, \rho\) and \(f\) are parameters from EAM potential [40]. The first and second terms on the right side of the above equation represent the thermal and atomic interactions respectively.

The local atomic structure is identified using centrosymmetry parameter (CSP) [51], which is defined as follows:

\[
p_i = \frac{1}{D_0} \sum_{j=1,6} |R_i + R_{ij}|^2
\]

(4)

where \(R_i\) and \(R_{ij}\) are the vectors corresponding to the six pairs of opposite nearest neighbors in the \(fcc\) lattice. \(D_0\) is the distance of the nearest neighbors. \(p_i\) is the CSP value of atom \(i\). In \(fcc\) structures, each atom has six pairs of opposite nearest neighbor atoms, i.e., six pairs of opposite bonds. In Fig. 2, there are three pairs of opposite bonds to illustrate the method. Under deformation or on a defect these bonds will change in length and direction and that change is quantified in a parameter. For reference, \(p_i < 0.4\) corresponding to \(fcc\) structure, especially \(p_i = 0\) reflect a perfect \(Cu\) lattice. \(0.7 < p_i < 1.2\) stand for stacking faults, that is \(hcp\) atoms. \(p_i > 1.8\) represent for surface atoms.

This study addresses tensile loading of Cu NWs with \(\{100\}\), \(\{110\}\) and \(\{111\}\) crystallographic orientations, respectively. Stress–strain curves are obtained to locate the initial yield points and to determine the plastic region of loading. The snapshots of the loading process are captured to understand the incipient plastic deformation mechanism of the NWs. In the next step, the behavior of Cu NWs is simulated at different temperatures.

3. Result and discussion

3.1. Anisotropic effects in elastic and incipient plastic deformation

Fig. 3 shows the stress–strain relationship of three different oriented NWs at \(T = 10 K\) and strain rate = 0.1% ps\(^{-1}\). As presented in Fig. 3, each curve increases up to a threshold stress value corresponding to a yield strain respectively. After the yield point, it is observed that the curves are nonlinear and saw-shaped in the inelastic region. Hence, the Young’s modulus is determined by applying a curve to fit the data in the elastic region. As is presented in Table 1, the difference of Young’s modulus is shown to have \(E_{\{111\}} > E_{\{110\}} > E_{\{100\}}\) for Cu NWs, indicating that the Young’s modulus is strongly dependent on the crystallographic direction. The calculated dependence relations are in good agreement with Au [38] and Ni [52] monocrystals in atomistic calculations. In addition, by comparison with the fracture strain of \(\{100\}\) and \(\{111\}\) Cu NWs, the \(\{110\}\) NW exhibits a low ductility, which was verified by HRTEM images of gold NWs [23].
The snapshots of the deformations of point A–E are shown in Fig. 6a–e, respectively. (c) The snapshots of the deformations of point A–D are shown in Fig. 8a–d, respectively. (b) The snapshots of the deformations of different NWs at 10 K (size: 10 × 10 × 40 unit-cell). From points B to C (ε = 8.7%), although only a slight increase in strain, the atomic rearrangements extend over many layers and cause a short of “domino effect”. Such a rearrangement process continues and brings the wire to a local minimum stress state at point D (ε = 9.5%), where two slip systems joint together in the NW interior. Meanwhile, the state at point D is also illustrated by a cutaway view of the NW in Fig. 5, where the deformation of twin is observed. In the sequential tensile loading process, the twinning deformation play an important role in the plastic deformation of (1 0 0) NW. By monitoring defects evolution of the NW during the whole tensile process, we further display the fraction of different categories of atoms as a function of the tensile strain (see Supporting information S1).

In Fig. 6, five snapshots are presented according to the five tagged points on the stress–strain curve in Fig. 3b. Beyond the elastic region in Fig. 6a, the (1 1 0) NW cannot keep the perfect fcc structure, and the first nucleation of dislocation at the corner of the surface is found at the yield point (point A in Fig. 3b). The partial dislocation traverses the cross section of the NW along a (1 1 1) slip plane and in doing so creates an intrinsic stacking fault in the fcc structure (Fig. 6a and b). After reaching the opposite surface, the stacking fault further propagate through the NW with the same manner along the tensile direction. As is shown in Fig. 6d, a distinct “N” shape slip plane is formed in the NW. It is not difficult to find that there is a stress plateau with a magnitude of 4.6 GPa between points D and E in Fig. 3b. The stress plateau extends for about 4.5% of strain, which is nearly equal to the strain of the elastic region. As is displayed in Fig. 6e, the long stress plateau in stress–strain curve leads to a large post-yield ductility, which results from the twinning-dominated behavior. For clarity, a cutaway view of point E is shown in Fig. 7. Two micro-twin bands exist on the left and middle part of the NW, which lead the formation of a small step on the surface. While another twin band on the right hand seems larger, and thus it leads to a relatively bigger surface step. Although (1 0 0) NW shows partial dislocation nucleation and the subsequent twinning process in plastic deformation which is similar to (1 0 0) NW, the decrease of fcc atoms shows a step-shaped manner during the whole inelastic deformation process, which is different from defects evolution of (1 0 0) and (1 1 1) NWs (see Supporting information S2).

<table>
<thead>
<tr>
<th>Nanowire's orientation</th>
<th>Young's modulus (GPa)</th>
<th>Yielding stress (GPa)</th>
<th>Yielding strain</th>
<th>Fracture strain</th>
<th>Schmidt factor, m_i</th>
<th>Schmidt factor, m_m</th>
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<td>(1 0 0)</td>
<td>100.16</td>
<td>7.43</td>
<td>0.080</td>
<td>0.597</td>
<td>0.23</td>
<td>0.47</td>
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<td></td>
<td>(80.04)</td>
<td>(4.51)</td>
<td>(0.056)</td>
<td>(0.477)</td>
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<tr>
<td>(1 1 0)</td>
<td>115.69</td>
<td>6.32</td>
<td>0.049</td>
<td>0.347</td>
<td>0.47</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>(102.30)</td>
<td>(4.15)</td>
<td>(0.041)</td>
<td>(0.335)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1 1 1)</td>
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<td>8.38</td>
<td>0.051</td>
<td>0.755</td>
<td>0.31</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>(137.58)</td>
<td>(4.88)</td>
<td>(0.037)</td>
<td>(0.624)</td>
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</tr>
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</table>

Table 1: The Young's modulus, Yielding stress, Yielding strain and the Schmidt factor for the leading (m_i) and trailing (m_m) partial dislocation for different NWs. The relevant mechanical parameters at room temperature are also listed in parentheses.

Fig. 3a illustrates the stress–strain relationship of (1 0 0) NW. The points (A) — (D) in Fig. 3a are related to a–d in Fig. 4. As can be seen in Fig. 3a, the stress drops abruptly beyond the elastic limit (point A), where the plastic deformation may generate near the surface (Fig. 4a). This slight contract of the surface atoms immediately induced new emerging Shockley partial dislocations in Fig. 4b (point B). From points B to C (ε = 8.7%), although only a slight increase in strain, the atomic rearrangements extend over many layers and cause a short of “domino effect”. Such a rearrangement process continues and brings the wire to a local minimum stress state at point D (ε = 9.5%), where two slip systems joint together in the NW interior. Meanwhile, the state at point D is also illustrated by a cutaway view of the NW in Fig. 5, where the deformation of twin is observed. In the sequential tensile loading process, the twinning deformation play an important role in the plastic deformation of (1 0 0) NW. By monitoring defects evolution of the NW during the whole tensile process, we further display the fraction of different categories of atoms as a function of the tensile strain (see Supporting information S1).
The (1 1 1) NW with two (1 1 2) and two (1 1 0) side surfaces is also performed by tensile loading. In Fig. 8, four snapshots are presented correspond to the four tagged points on the stress–strain curve in Fig. 3c. Upon reaching the first yield strain of $\varepsilon = 5.1\%$, the defect begin to initiate at the top of the (1 1 0) surfaces (Fig. 8a). Two parallel stacking faults named $\alpha$ and $\beta$ plane continue to propagate in snapshots of Fig. 8b and c. The partial dislocation of $\alpha$ plane reaches one end of the NW firstly, which lead to two slip planes crisscross in the interior of the NW. When the induced slip further reaches the bottom (1 1 0) surface, another (1 1 1) glide surface ($\gamma$ plane) emerges at the bottom and emits to the opposite surface (Fig. 8d). These snapshots demonstrate that the dislocations are nucleated at surface edges and lead to a glide surface. Unlike the results of (1 0 0) and (1 1 0) NWs, we did not observe clear twinning deformation during the tensile process. For the whole defects evolution from its initial state to complete rupture, please refer Supporting information S3.

An important factor in evaluating the plastic deformation of bulk single crystal under tensile loading is Schmidt factor. As is known to all, the plastic deformation mode in bulk crystal depends on the relationship between the Schmidt factor of the leading partial dislocation ($m_l$) and the trailing partial dislocation ($m_t$). In the initial yielding, a (1 1 2) leading partial dislocation nucleates on a (1 1 1) plane. In the next step, if $m_t$ is less than $m_l$ then another (1 1 2) leading partial dislocation on adjacent parallel (1 1 1) plane forms easily. Therefore, twinning is favored under this condition, while full dislocation slipping is preferred under the reverse condition ($m_t > m_l$) [54,55]. From a crystallographic viewpoint, partial dislocation motion and twinning would be favored in tensile loaded (1 1 0) and (1 1 1) wires as seen in Table 1. On the other hand, the motion of pure slip is relatively preferred in tensile loaded (1 0 0) wires. In this study, MD simulation confirmed the twinning deformation behavior of (1 1 0) as seen in Fig. 7. However, we did not observe clear twinning deformation in the NW. Only twinning-like, parallel stacking faults was seen in loaded (1 1 1) NW. In (1 0 0) NW, the full dislocation slip as well as twinning is the primary plastic deformation mechanism, as indicated in Fig. 5. Consequently, it can be concluded from above discussion that the Schmidt factor of bulk single crystal is valid for (1 1 0) Cu NW but invalid for tensile loaded (1 0 0) and (1 1 1) NWs, reflecting that the loading rate and surface effects may also play a role in the failure model during Cu NWs tensile loading [54].

3.2. Temperature effect on the stability of tensile loaded NWs

The behavior of Cu NW is simulated at different temperatures (temperature varies between 10 K and 450 K. For simplicity, we choose (1 0 0) NW as representative). The stress–strain curves of (1 0 0) NW with different temperatures are given in Fig. 9a. At lower temperature of $T = 10$ K, the stress–strain curve displayed in a smaller amplitude and clear peaks manner. While at of $T = 450$ K, The stress–strain curve vibrates at much larger amplitude as compared to other curves. This may imply that the atomic structure has higher entropy, and thus atoms have much larger oscillations about their equilibrium positions. As is shown in Fig. 9b, the Young’s modulus is very sensitive to the increase of temperature. For instance, the Young’s modulus of room temperature is about 20% smaller than the NW at 10 K. This trend may associate with
the significantly weaken of bond forces and can be compared with the simulation results of Au NWs [54] and experimental measurements [56,57]. Generally, the Young’s modulus decreases nearly linearly with the increase of temperature. The theoretical reason is as follows. According to the definition of Young’s modulus, the first derivative of the potential with respect to equilibrium distance \( r \) is analogous to Young’s modulus. If one considers the first derivative of Lennard–Jones potential, the deduction process may be simplified, and thus the Young’s modulus is proportional to \( 1/r^2 \). As a result, with the increase of temperature, the equilibrium distance of atom position is increased. This induces the decline of Young’s modulus. Therefore, both the variation of stress–strain curves and the drop of Young’s modulus indicate the less stable crystal structure as increasing of temperature.

To substantiate the thermal effect on Cu crystal structure under tensile loading, we presented two snapshots of tensile loaded \( \{1 0 0\} \) NW at 450 K in Fig. 10, which correspond to the stress–strain curve in Fig. 9a. Fig. 10a and b is related to the yield point \( (\varepsilon = 6.0\%) \) and the first minimum stress state \( (\varepsilon = 7.8\%) \), respectively. It was observed that there are much more non-fcc atoms at \( T = 450 \) K as compared to \( T = 10 \) K (Fig. 4a) at the yield point, which indicates the relative instability of crystal structure due to a higher temperature. By comparing defects evolution in Fig. 10b and Fig. 4d, it seems that the temperature has no substantial effects on the plastic deformation mechanism of Cu NWs. We further display the radius distribution function (RDF) analysis of copper NWs corresponding to different temperatures in Fig. 11. The RDF functions at different temperatures in Fig. 11 are corresponding to their first minimum stress states in stress–strain curves (Fig. 9a). The peaks in the RDF became wider and lower with the increase of temperature. Nearly all the peaks vanished in \( T = 450 \) K except for the first peak in the RDF, which suggests the presence of disorder in the NW.
4. Conclusions

In conclusion, we have studied the influence of different crystallographic orientations and temperatures on the mechanical deformation behavior of copper NWs under tensile loading. Our studies stress the effects of crystallographic orientation on Young’s modulus, yield behavior and incipient plastic deformation of Cu NWs. The centrosymmetry parameter is used to investigate the structure evolution and deformation behavior of Cu NWs. Both the elastic properties and plastic properties are found to be orientation dependent. The difference of Young’s moduli is shown as $E_{110} > E_{111} > E_{100}$ for Cu NWs. For tensile loaded (1 0 0) NW, both slip and twinning deformation behavior were seen in the wire. For tensile loaded (1 1 1) NW, the MD simulation results showed the twinning-dominated deformation mechanism, which confirmed the trend of Schmidt factor. For (1 1 1) NW, we did not observe clear twinning deformation in the NW.

In this study, we also obtained some evidence from our simulations that by raising the temperature, the stress-strain curve vibrated at much larger amplitude. The yield stress and the Young’s modulus were decreased with the increase of temperature.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1106/j.computmatsci.2011.05.023.

References