Influence of Grain Boundaries on the Vibrational Properties of Silver Nanowires

H.F. Zhan\textsuperscript{1}, Y.T. Gu\textsuperscript{*1}, C. Yan\textsuperscript{1}, and Prasad K.D.V. Yarlagadda\textsuperscript{1}
\textsuperscript{1}School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology, Brisbane, QLD 4001, Australia
\textsuperscript{*Corresponding author: yuantong.gu@qut.edu.au}

Abstract
Metal and semiconductor nanowires (NWs) have been widely employed as the building blocks of the nanoelectromechanical systems, which usually acted a resonant beam. Recent researches reported that nanowires are often polycrystalline, which contains grain boundaries (GBs) that transect the whole nanowire into a bamboo like structure. Based on the larger-scale molecular dynamics (MD) simulations, a comprehensive investigation of the influence from grain boundaries on the vibrational properties of doubly clamped Ag NWs is conducted. It is found that, the presence of grain boundary will result in significant energy dissipation during the resonance of polycrystalline NWs, which leads a great deterioration to the quality factor. Further investigation reveals that the energy dissipation is originated from the plastic deformation of polycrystalline NWs in the form of the nucleation of partial dislocations or the generation of micro stacking faults around the GBs and the micro stacking faults is found to keep almost intact during the whole vibration process. Moreover, it is observed that the closer of the grain boundary getting to the regions with the highest strain state, the more energy dissipation will be resulted from the plastic deformation. In addition, either the increase of the number of grain boundaries or the decrease of the distance between the grain boundary and the highest strain state region is observed to induce a lower first resonance frequency. This work sheds lights on the better understanding of the mechanical properties of polycrystalline NWs, which benefits the increasing utilities of NWs in diverse nano-electronic devices.

Keywords: grain boundary, vibration, nanowire, quality factor, molecular dynamics.

1. Introduction
Metal and semiconductor nanowires (NWs) have been widely utilized as active components of nanoelectromechanical systems (NEMS) due to their extraordinary mechanical, electrical, optical and thermal properties, such as high frequency resonators, field effect transistors (FETs), and other devices (Xie et al., 2011). Hence, a comprehensive understanding of the mechanical properties of NWs is increasingly required. There have been a number of experimental, theoretical and computational studies on the properties of NWs. On the experimental front, researchers have studied the mechanical behaviors of NWs under bending, tension, compression and vibration. On the theoretical and computational front, either surface-based extensions of
Continuum elasticity theory (Wang and Feng, 2009) or multi-scale computational techniques (Park and Klein, 2008) has been employed to investigate the mechanical properties of NWs. Besides, molecular dynamics (MD) simulations is also being frequently adopted to explore structure-property relationship for NWs under different loading conditions (Park and Zimmerman, 2005; Zhan and Gu, 2012a; Zhan and Gu, 2012c; Zhan and Gu, 2012b).

It is noticed that most of current studies have focused upon perfect NWs due to the decreased possibility of defects and flaws in nanoscale materials. However, recent experimental studies reveal that NWs also contain certain defects. For instance, metal NWs are found usually polycrystalline, containing grain boundaries (GBs) that transect the whole NW normal to its longitudinal axis into a bamboo structure (Bietsch and Michel, 2002). Lopez et al. (Lopez et al., 2009) reported the existence of ordered stacking fault arrays in Si NWs, and (001) stacking defects are also observed to intersperse with small cubic GaN regions in the GaN NW (Tham et al., 2006). Furthermore, twin boundaries are considered as ubiquitous for both synthesis and properties in nano-enhanced FCC metals. Therefore, it is crucial to characterize the mechanical properties of NWs with different defects.

There have been a number of studies on the mechanical behaviors of defected NWs. For example, a serial of investigation on the twinned Cu NWs under tensile deformation has been conducted by Cao and his group members (Cao and Wei, 2006). Au and other metal NWs with twin boundaries have also been extensively studied by Sansoz and his group members (Deng and Sansoz, 2009). Several works regarding the influence of pre-existing defects on the mechanical properties of metal NWs under tension (Zhan and Gu, 2011a; Zhan et al., 2011a), torsion (Zhan et al., 2011b) and compression (Zhan and Gu, 2011b) has also been reported recently. Since NWs commonly play a role of a vibrating beam in NEMS, under such schematic very minute changes in the local environment, e.g., perturbations in forces, pressure or mass, can be detected by monitoring the corresponding changes in the resonance frequency of the NW (Kim and Park, 2008). However, it is found that majority of current studies have emphasized on the mechanical properties of NWs under uniaxial loading conditions, and the study of the influence from different defects on the resonant properties of NWs is still lack in the current literature. Thus, we perform a comprehensive investigation of the influence from GBs on the vibrational properties of Ag NWs using large-scale MD simulations in the present work.

2. Numerical details

Large-scale MD simulations were carried out on bamboo-like polycrystalline Ag NWs with square cross-section, which were generated according to the work by Cao et al. (Cao et al., 2008), i.e., the <100> crystalline direction is chosen as the misorientation axis, and the GBs separating individual grains are \( \sum 5(310)36.9^\circ \) symmetric high-angle tilt GBs, which has a high density of coincident atomic sites across the interface. This structure has also been experimentally observed (Merkle, 1995) and studied using numerical simulations (Cao, Wei et al., 2008) by previous researchers. We considered a serial of NWs contain different number of GBs with an identical size (4.91×5.17×52.77 nm\(^3\)). Specifically, GBs number including 0, 1, 3, 4 and 9 were considered, which leads the grain boundary spacing (GBS) ranging from 5.17-12.93 nm (that is comparable to the experimentally investigated grain size of 5-
40 nm). We modelled Ag using the embedded-atom-method (EAM) potential developed by Foiles et al. (Foiles et al., 1986). This potential was fitted to a group of parameters, including cohesive energy, equilibrium lattice constant, bulk modulus, and others including a lattice constant $a$ which is chosen as 0.409 nm (Voter, 1993).

During each simulation, the NW was first created assuming bulk lattice positions, and then relaxed to a minimum energy state using the conjugate gradient algorithm, i.e. the length of the NW was allowed to decrease in response to the tensile surface stress. We then used the Nose-Hoover thermostat (Nosé, 1984; Hoover, 1985) to equilibrate the NW at a constant temperature 10 K (NVT ensemble) for 400 ps at a time step of 4 fs while holding the newly obtained length of the NW fixed. Finally, the NWs are actuated by applying a sinusoidal velocity excitation $v(z) = \lambda \sin(kz)$ along the lateral direction ($x$-axis), where $\lambda$ is the actuation amplitude, and $k = \pi / L$. As illustrated in Fig. 1a, the two ends of the NW are fixed in all three directions to mimic a doubly clamped beam. No periodic boundary conditions were utilized at any point during the simulation process.

During the vibration process, the NW is modeled using the microcanonical (NVE) ensemble following the velocity actuation, and that the applied velocity field increased the total potential energy by less than 0.1%, which ensures that the oscillations occur in the linear regime. The overall simulation methodology to study the oscillatory properties of the NWs is identical to that used previously for metal NWs (Kim and Park, 2009; Zhan and Gu, 2012a). All simulations were performed using the open-source LAMMPS code developed at Sandia National Laboratories (Plimpton, 1995). In order to recognize the defects in NWs, the centro-symmetry parameter ($csp$) (Kelchner et al., 1998) is utilized, which increases from zero for perfect FCC lattice to positive values for defects and for atoms close to free surfaces.

![Figure 1](image.png)

**Figure 1.** (a) A doubly clamped polycrystalline Ag NW containing three GBs with a square cross-section. ‘E’ represents the fixed end. (b) The profile of a sinusoidal velocity actuation.

### 3. Results and discussion

Following studies focus on the discussions on the quality ($Q$)-factor and natural (resonance) frequency of the polycrystalline Ag NW. $Q$-factor is a crucial parameter to assess the sharpness of a resonance curve, which is typically defined as the ratio between the total system energy and the average energy loss in one radian at resonant frequency (Bao, 2005), that is $Q = 2\pi E / \Delta E$, where $E$ is the total energy of the vibration system and $\Delta E$ is the energy dissipated by damping in one cycle of vibration. Assume $Q$-factor is constant during vibration, then after $n$ vibration cycles, the maximum energy $E_n$ is related to the initial maximum energy $E_0$ by (Jiang et al., 2004) $E_n = E_0(1 - 2\pi / Q)^n$. Due to the microcanonical (NVE) ensemble adopted during NW oscillation, the loss of potential energy must be converted to the kinetic
energy. Thus, the time history of the external energy (EE) will be tracked for the calculation of Q-factor, which is defined as the difference of potential energy before and after the transverse velocity is applied to the NW (Kim and Park, 2008). To determine the vibration frequency from the simulation results, the fast Fourier transform (FFT) (Brigham and Morrow, 1967) is applied.

3.1 Ag NWs with evenly distributed GBS

Vibration tests were firstly carried out on polycrystalline Ag NWs with evenly distributed GBS, i.e., the distance between GBs or the NW’s clamped ends is an identical value (see Fig. 1a). The actuation is imposed along x-axis (that is <001> direction), and the actuation magnitude is the same for all tested NWs (\( \lambda = 0.4 \) Å/ps). Fig. 2 presents the time history of EE obtained from polycrystalline NWs with 0, 1, 3 and 9 GBs. For the perfect NW, the gradual changing of the EE amplitude indicates that the nonlinear vibration has not been excited. The Q-factor is estimated around \( 3.7041 \times 10^4 \), which is comparable with the value reported by previous researchers (Kim and Park, 2008; Zhan and Gu, 2012a). The most striking feature of the mechanical response of the polycrystalline NW is the highly nonlinear nature of the EE amplitude. From Fig. 2b, 2c and 2d, we found EE amplitude has received an evident attenuation due to the presence of GBs. For the NW with one GB, EE amplitude decays linearly and rapidly along with time, and the Q-factor is estimated only about 778.09 (in Fig. 2a). Meanwhile, for NWs with more GBs, larger attenuation of the EE amplitude is observed at the beginning of oscillation, which behaves as a reciprocal function of time. Following the initial attenuation, the EE amplitude of the NW with three GBs (Fig. 2c) is found to decrease gradually with the increase of time. Similar trajectory of the external energy versus time is also obtained from the NW with nine GBs (Fig. 2d), whose amplitude shows an even narrower variation scope after the initial attenuation. Therefore, it is found that the presence of GBs will result in great energy dissipation during the resonance of polycrystalline NWs. To probe the underlying mechanisms of this phenomenon, further analysis were conducted as below.

Fig. 3 represents the atomic configurations of the NW with four GBs at the time of 0, 1.2 and 6 ns. According to Fig. 3a, the NW possesses four perfect GBs after relaxation. However, after the introduction of the initial actuation, the nucleation of partial dislocations and the generation of micro stacking faults are observed around the corner of the GBs (Fig. 3b). It is interesting to found that the configurations around GBs are almost the same with the increase of time. As seen in Fig. 3c, the micro stacking faults around the GBs appears almost unchanged at the time of 6 ns.

**Figure 2.** Time history of EE for different NWs with a testing duration of 11.6 ns. a) perfect NW; b) NW with one GB; c) NW with three GBs; d) NW with nine GBs.
comparing with those at the time of 1.2 ns, which suggests that these micro stacking faults are nearly intact during the whole vibration process.

![Image](image1.png)

**Figure 3.** Atomic configurations of the NW with four GBs during vibration test. a) After relaxation; b) At the time of 1.2 ns; c) At the time of 6 ns.

To track the deformation process during vibration, the csp value for each atom is also calculated. Particularly, atoms with csp between 0.5-12 are regarded as partial dislocation \((0.5 < \text{csp} \leq 3)\) or stacking faults atoms \((3 < \text{csp} \leq 12)\) (Zhan, Gu et al., 2011a). For discussion convenience, these atoms are referred as dislocation atoms, and the relative dislocation atoms number \(dN_r\) is defined as \(dN_r = N_0 - N_t\), where \(N_0\) is the dislocation atoms number after relaxation (before applying the actuation) and \(N_t\) is the dislocation atoms number at the time of \(t\). Fig. 4 shows the time history of both \(EE\) and \(dN_r\) for the NW with four GBs. In accordance with the initial decay of the \(EE\) amplitude at the onset of vibration, the corresponding time history of \(dN_r\) reveals a sharp increase, after which, \(dN_r\) is found to fluctuate around 140. Comparing with the atomic configurations in Fig. 3, the sharp increase region of \(dN_r\) is actually related with the occurrence of plastic deformation in the form of the nucleation of partial dislocations or the generation of micro stacking faults. In the meanwhile, the fluctuation region implies that the plastic deformation is relatively stable during the following vibration process, which approved the previous arguments that the micro stacking faults are nearly unchanged with the continuing resonance of the NW. Hence, it could be concluded that, the initial attenuation of the external energy is induced by the energy dissipation, which is originated from the occurrence of the plastic deformation around the GBs. Furthermore, the micro stacking faults keep almost intact during the whole vibration process.

![Image](image2.png)

**Figure 4.** Time history of \(EE\) and \(dN_r\) for the Ag NW with four GBs.

### 3.2 Ag NWs with unevenly distributed GBS

Following interests are laid on the influence from unevenly distributed GBS, we took the NW with three GBs as the testing sample. Specifically, the distance \((d)\) between
GBs 1 and 2 or 3 and 2 is kept the same, which varies from 10a, 20a, 30a, and 40a, where a is the lattice constant along the <310> direction (see Fig. 1a).

Figure 5 presents the time history of EE for the four different polycrystalline NWs. In general, the distance d exerts significant influence on the mechanical response of the NW. It is observed that in Fig. 5a and 5d, the EE amplitude shows a significant attenuation at the early stage of vibration and then fluctuates within a narrow scope. This phenomenon indicates that more plastic deformation is emerged in these two cases comparing with the NW with evenly distributed GBS (in Fig. 2c). According to Figs. 5c and 5d, the value of dNt for the polycrystalline NW with d = 30a fluctuates around 90, while for the NW with d = 40a it fluctuates around 110, which affirms that more plastic deformation is occurred to the latter NW. It is known that for a NW under bending deformation, the two end regions as well as the middle region are under the highest strain state (Zhan and Gu, 2012c). Therefore, it is reasonable to observe more energy absorbed by the generation of partial dislocations or stacking faults when the GB is getting closer to these three regions, and hence induce a great attenuation to the external energy.

![Figure 5](image)

**Figure 5.** MD results for NWs contain unevenly distributed GBs with a testing duration of 11.6 ns. a) Time history of EE for NW with d = 10a; b) Time history of EE for NW with d = 20a; c) Time history of EE and dNt for NW with d = 30a; d) Time history of EE and dNt for NW with d = 40a.

We close this work by the discussion of the first resonance frequency as obtained from the time history of the external energy for each considered NW. Fig. 6a shows the first resonance frequency for the polycrystalline NWs with evenly distributed GBS. Just as expected, the frequency is found to experience an obvious decrease with the increasing number of GBs. Meanwhile, for the polycrystalline NWs with unevenly distributed GBS, the frequency shows a parabolic relation with the distance d, which is consistent with previous argument that the closer of the GBs to the three highest strain state regions, the larger influence will be resulted.
Figure 6. The first natural frequency of the tested NWs as obtained using FFT. a) NWs with different number of GBs; b) NWs with unevenly distributed GBS.

4. Conclusion

Based on the larger-scale MD simulations, the influence of grain boundaries on the vibrational properties of doubly clamped Ag NWs is investigated. Polycrystalline NWs are modeled with evenly or unevenly distributed grain boundaries. Major conclusions are summarized as below:

1) The presence of grain boundary will result in significant energy dissipation during the resonance of polycrystalline NWs, which leads a great deterioration to the Q-factor. Specifically, the external energy will receive an obvious attenuation at the early stage of vibration then oscillate within a relative narrow scope.
2) The energy dissipation is originated from the plastic deformation of polycrystalline NWs in the form of the nucleation of partial dislocations or the generation of micro stacking faults around the GBs. Moreover, the micro stacking faults is found to keep almost intact during the whole vibration process.
3) It is found that the closer of the grain boundary getting to the regions with the highest strain state, the more energy dissipation will be resulted from the plastic deformation.
4) Either the increase of the number of grain boundaries or the decrease of the distance between the grain boundary and the highest strain state region is found to induce a lower first resonance frequency.

This work presents a first investigation on the influence from grain boundaries on the vibrational properties of NWs, which sheds lights on the better understanding of the mechanical properties of polycrystalline NWs. The study would benefit the increasing utilities of NWs in diverse nano-electronic devices.

Acknowledgement

The authors heartily appreciate Professor Harold S. Park at Boston University for his insightful suggestions in preparing this paper. In addition, this work is supported by the ARC Future Fellowship grant (FT100100172).

References


