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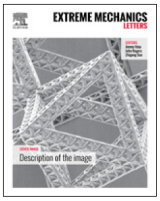

On the size-dependent elasticity of penta-twinned silver nanowires

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Penta-twinned metallic NWs have recently received much attention due to their excellent mechanical properties. However, their elasticity size effect remains not well understood due to the large discrepancy in the reported experimental and simulation results. This paper reports an experimental effort to address the discrepancy about the size-dependent Young's modulus of penta-twinned Ag NWs. Two independent experiments on the same NW, *in-situ* resonance test and tensile test in a scanning electron microscope, were used to measure the Young's moduli. The cross-sectional shape of the Ag NWs was found to transit from pentagon to circle with decreasing NW diameter, which can modify the Young's modulus as much as 8% (for resonance test) and 19% (for tensile test) for the tested diameter range. This work confirmed that the Young's modulus of penta-twinned Ag NWs increases with decreasing NW diameter.

1. Introduction

Recent advance in nanotechnology has brought forth a host of nanomaterials, such as nanoparticles, nanowires (NWs), nanotubes and 2D nanomaterials that exhibit ultrahigh mechanical strength [1,2]. Such nanomaterials not only are building blocks for a broad range of nanomaterial-enabled applications, but also provide ideal platforms for studying fundamental mechanical behaviors at the nanoscale. As an example, metallic NWs have shown promising potential for flexible/transparent electronics and stretchable electronics [3,4]; their deformation mechanism is now known to transit from forest dislocation dynamics to dislocation nucleation from free surfaces [5–7].

A variety of metallic NWs can be synthesized now using several methods including electrochemical deposition [8] and physical vapor deposition [9,10]. Among all the metallic NWs, penta-twinned NWs are unique in microstructure—each NW has five twin segments joined along a common quintuple line in the axial direction. In addition, synthesis of penta-twinned metallic NWs based on solution phase is relatively easy and scalable [11]. Penta-twinned metallic NWs have recently received much attention due to their excellent mechanical properties. For instance, increased Young's modulus and yield strength with decreasing NW diameter have been recently reported [6,12]. More recently, recoverable plasticity [13,14] and strain hardening [15] have been investigated.

However, the elasticity size effect of penta-twinned metallic NWs is still under debate. Both experimental and modeling results on the Young's modulus of penta-twinned Ag NWs, as an example, exhibited large discrepancies. Using *in-situ* tensile tests in scanning or transmission electron microscopy (SEM/TEM), Zhu et al. [6] and Filleter et al. [12] reported pronounced stiffening effect, i.e., increased Young's modulus with decreasing NW diameter. Using bending tests under atomic force microscopy (AFM), Jing et al. [16] found a similar stiffening effect to the above tensile tests. In contrast, Wu et al. [17] obtained an average

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Young's modulus that is higher than the bulk value but independent of the NW diameter; Chen et al. [18] reported Young's moduli that are higher than the bulk value but without obvious size effect, similar to the result by Alducin et al. [19] using *in-situ* TEM bending. In all the experiments above, the NWs were ⟨110⟩ oriented with diameters typically between 20 and 140 nm. However, no experiments compared the Young's moduli of the penta-twinned Ag NW and the single-crystalline counterpart.

Atomistic simulations showed pronounced stiffening size effect but no significant effect of the penta-twinned microstructure compared to the single-crystalline counterpart [20,21]. Other atomistic simulations revealed the similar size effect, but also showed strong effect of the penta-twinned microstructure, leading to higher Young's modulus than that of the single-crystalline NW [22,23]. The microstructure effect was attributed to the high compressive at the core of the penta-twinned NW. Similar conclusions on the size and microstructure effects were observed in other penta-twinned FCC NWs, such as Cu, Au, Ni, Pd and etc. [24,25]. More recently, Bitzek and co-workers carried out a systematic study on the Young's modulus of several types of FCC penta-twinned NWs using atomistic simulations and analytical modeling [26]. They found that while the size effect is atomic origin (e.g., surface stress and surface elasticity), the effect of the penta-twinned microstructure is due to compatibility constraint imposed by the microstructure and elastic anisotropy of the FCC metal.

The elasticity size effect can be generally attributed to two mechanisms [27]: surface elasticity [28–32] and bulk nonlinear elasticity (as a result of the surface stress) [33]. Under different loading modes, the elasticity size effect manifests differently for different mechanisms [21,28,34]. For instance, in the case of surface elasticity, the elasticity size effect would be stronger under bending than under tension as the surface plays a more important role under bending. More specifically, the NW Young's modulus $E = E_c + 8\frac{S}{D}$ and $E = E_c + 4\frac{S}{D}$, respectively, under bending and tension, where E_c is the Young's modulus of the core and D is the NW diameter [34]. Therefore, for probing the underlying mechanism of the elasticity size effect, it is valuable to obtain the Young's modulus under different loading modes. Zhu and co-workers measured the elasticity size effect of ZnO NWs under both tension and buckling [34]. However, since the buckling force and hence the measured Young's modulus sensitively depend on the NW diameter (4th power in contrast to square in the case of tension), the buckling method could lead to larger error in measuring the Young's modulus compared to other methods such as tension and resonance [35].

This paper reports an experimental effort to address the discrepancy about the size-dependent Young's modulus of penta-twinned Ag NWs. Two independent experiments on the same NW, *in-situ* SEM resonance test and tensile test, were used to measure the Young's moduli. In addition, the cross-sectional shape of the Ag NWs was measured as a function of the NW diameter, which was found to transit from pentagon to circle with decreasing NW diameter. The effect of the cross-sectional shape on the measured Young's modulus was evaluated. This work confirmed that the Young's modulus of penta-twinned Ag NWs increases with decreasing NW diameter, though the size effect is less pronounced compared to our previous result [6].

2. Materials and methods

Penta-twinned Ag NWs were synthesized by reducing $AgNO_3$ with ethylene glycol in the presence of polyvinyl pyrrolidone. More details of the NW synthesis process are provided elsewhere [6,11]. The solution of Ag NWs was diluted with deionized water and then purified by centrifugation.

In-situ resonance and tension tests of the same NWs were carried out inside a dual beam SEM/FIB system (FEI Quanta 3D FEG) using a two-probe setup. The first probe was glued on a piezoelectric sheet that was used to provide mechanical vibration. The second probe was installed on a nanomanipulator (Klocke Nanotechnik, Germany) for manipulating an individual NW including picking up from substrate and mounting onto a MEMS stage. After the NW was transferred from the second to the first probe and clamped using electron beam induced deposition of platinum (EBID-Pt), the piezoelectric sheet was excited into mechanical vibration (Fig. 1(a)). Note that the clamping condition was inspected carefully following [36] in order to obtain the Young's modulus accurately. As soon as the frequency of AC signal was close to the resonance of NW, the vibration amplitude of NW increased sharply, as shown in Fig. 1(b). Around the resonance frequency of the NW, SEM images of the vibrating NW were taken at a number of frequencies, from which the vibration amplitude was measured as a function of the frequency (Fig. 2(a)). Then the resonance frequency can be determined from the amplitude–frequency plot. After the resonance test, the NW was transferred from the first probe back to the second probe (attached to the nanomanipulator) for the *in-situ* tensile testing. For more details of transferring a NW, please see Supporting Information.

Prior to the tensile testing, the NW on the second probe will be further transferred to a microelectromechanical system (MEMS) stage following [37]. The MEMS stage consists of a thermal actuator, a capacitive load sensor and a gap in between where the NW will be mounted. The MEMS stage was fabricated at MEMSCAP (Durham, NC) using the Silicon-on-Insulator Multi-User MEMS Processes (SOI-MUMPs). The strain rate was nominally 10^{-4} s^{-1}. Details of performing *in-situ* tensile testing using the MEMS stage can be found elsewhere [13,38].

Cross-section TEM samples were prepared by embedding Ag NWs into Gatan G1 epoxy with a $\varphi 3$ Cu tube, cutting the specimen discs with a thickness of ∼0.5 mm, mechanically polishing with Allied Multiprep System and finally ion milling the sample via Gatan 791 PIPS while cooling with liquid nitrogen.

3. Results and discussion

From Fig. 2(a), the first resonance frequency of the penta-twinned Ag NW was identified as 799 kHz, which was then converted to the Young's modulus assuming a pentagonal cross section of the Ag NW. According to a

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