

High Strain Rate Tensile Testing of Silver Nanowires: Rate-Dependent Brittle-to-Ductile Transition

Rajaprakash Ramachandramoorthy,^{†,‡} Wei Gao,^{†,‡} Rodrigo Bernal,[†] and Horacio Espinosa^{*,†,‡}

[†]Department of Mechanical Engineering, Northwestern University, Evanston, Illinois 60208-3111, United States

[‡]Theoretical and Applied Mechanics Program, Northwestern University, Evanston, Illinois 60208-3111, United States

Supporting Information

ABSTRACT: The characterization of nanomaterials under high strain rates is critical to understand their suitability for dynamic applications such as nanoresonators and nanoswitches. It is also of great theoretical importance to explore nanomechanics with dynamic and rate effects. Here, we report in situ scanning electron microscope (SEM) tensile testing of bicrystalline silver nanowires at strain rates up to 2/s, which is 2 orders of magnitude higher than previously reported in the literature. The experiments are enabled by a microelectromechanical system (MEMS) with fast response time. It was identified that the nanowire plastic deformation has a small activation volume (<10 b^3), suggesting dislocation nucleation as the rate controlling mechanism. Also, a remarkable brittle-to-ductile failure mode transition was observed at a threshold strain rate of 0.2/s. Transmission electron microscopy (TEM) revealed that along the nanowire, dislocation density and spatial distribution of plastic regions increase with increasing strain rate. Furthermore, molecular dynamic (MD)



simulations show that deformation mechanisms such as grain boundary migration and dislocation interactions are responsible for such ductility. Finally, the MD and experimental results were interpreted using dislocation nucleation theory. The predicted yield stress values are in agreement with the experimental results for strain rates above 0.2/s when ductility is pronounced. At low strain rates, random imperfections on the nanowire surface trigger localized plasticity, leading to a brittle-like failure.

KEYWORDS: nanowire, bicrystalline, flexible electronics, nanoswitches, rate effects, nanoscale plasticity, dynamic testing, tension test, nanostructure

Tanomaterials such as nanowires and nanotubes are N anomaterials such as manomaterials and nano-envisioned to be used in NEMS platforms and nanoelectronics, where the frequencies of operation range from kHz to MHz. Despite a decade of research in nanomechanical testing, high strain rate behavior of nanomaterials remains widely unexplored. Experimental characterization of nanomaterials has been limited to strain rates from $10^{-5}/s$ to $10^{-1}/s$, ¹⁻³ with the majority of the rate-dependent experiments conducted under compressive loads on face centered cubic (FCC) nanostructures, e.g. nanopillars, as summarized in Figure 1. Designing and conducting nanomechanical testing at different strain rates under tensile loads is more complex^{4,5} as it often requires specialized micro electro mechanical system (MEMS) based testing platforms.⁶ Typically, the tensile testing platforms have been used to conduct nanomechanical tests at strain rates only up to $0.01/s^2$ as testing at higher strain rates requires faster actuation, fast-response load cells and faster data acquisition systems with nanoscale resolution. Thus, the deformation mechanisms of nanowires at strain rates above 0.01/s, especially at diameters in the sub-100 nm range, remains unknown. In the present study, we increased the tensile strain rate up to 2/s using a MEMS device capable of in situ scanning electron microscope (SEM) testing. The increased strain rate allows us to observe a brittle-toductile failure transition in bicrystalline silver nanowires.



Figure 1. Summary of the nanomechanical testing conducted at different strain rates and their respective size scales (Pd nanowires (NW) tension,¹ Ni NW tension,² and Cu nanopillars (NP) compression³).

Another motivation for high strain rate testing of nanowires, is to bridge the gap between nanoscale experiments and molecular dynamics (MD) simulations. Limited by computational

Received:September 9, 2015Revised:October 26, 2015Published:November 5, 2015

resources, MD simulations of nanowires are normally conducted at strain rates varying from $10^7/s$ to $10^9/s$, which is at least 10 orders of magnitude higher than the quasistatic experimental strain rates (typically $10^{-4}/s$). Because of this mismatch, some experimental results cannot be directly compared to the MD results. Although transition state theory^{7–9} can be used to link experimental and MD results, the comparison across 10 orders of magnitude raises questions, as later discussed. Here, upon increasing the experimental strain rates to 2/s, we are able to combine MD with theoretical and experimental analysis to explain the observed brittle-to-ductile transition. Moreover, we demonstrate a path for increasing experimental strain rates to approach those in MD simulations, which ultimately can become a powerful approach to validate MD empirical potentials.^{10,11}

As a case study for high strain rate testing of nanostructures, we chose silver nanowires because they have been proposed to replace indium tin oxide (ITO) in a multitude of flexible electronic applications such as touch panels, solar cells, and public displays owing to their superior electrical properties and low cost production and processing.¹² In all these applications, the silver nanowires are subject to a variety of loadings, possibly at different strain rates. The silver nanowires are typically synthesized using liquid-solution-based polyol processes, which produce two possible crystal structures: bicrystalline and pentatwinned.¹³ Previous research^{14–17} on silver nanowires mainly focused on the penta-twinned structure, which exhibits many interesting properties such as the anomalous Bauschinger effect and recoverable plasticity.¹⁶ However, the experimental characterization of structural and mechanical properties of bicrystalline silver nanowires in both quasistatic and high strain rate regimes remains mostly unexplored. In fact, differences in the mechanical deformation between penta-twinned and bicrystalline silver nanowires may lead to choosing one over the other depending on the expected strains and rates in a particular application. The in situ experiments presented here contribute fundamental information that can be used for such device-design decisions.

In this work, we report in situ SEM tensile tests on bicrystalline silver nanowires with diameters \sim 35–40 nm tested at strain rates spanning 5 orders of magnitude from 2 × 10⁻⁴/s to 2/s. We observed a strong rate-dependent plastic behavior, in particular, a brittle-to-ductile failure transition at 0.2/s strain rate. A brittle failure at low strain rates is caused by deformation localization from surface defect sites resulting from the nanowire synthesis process. Beyond 0.2/s strain rate, the nanowires display pronounced ductility with strain hardening and grain boundary migration, as revealed by both experiments and MD simulations. Meanwhile, the yield stress predicted from dislocation nucleation theory compares closely to experimental data in the strain hardening plastic regime.

New Methodology for High Strain Rate Tensile Testing. For tensile testing of nanostructures, we employ a MEMS consisting of a thermal actuator (TA) and a load sensor (LS), as shown in Figure 2. Due to joule heating and the V-shaped geometry of the beams,^{18,19} the actuator prescribes a controlled in-plane displacement when voltage is applied. Load is measured electronically by means of a load sensor (LS) of known stiffness, consisting of capacitive sensing fingers, whose displacement results in a change in capacitance, which can in turn be used to compute the force acting on the nanowire. (For detailed experimental methodology, see Supporting Information (SI) Discussion S1.) This device has been used previously for tensile testing of a variety of nanostructures at quasistatic strain rates,



Figure 2. Schematic of the MEMS testing platform (red arrow points to the actuation direction, scale bar is $250 \ \mu m$).

including metallic nanowires,^{16,17} semiconducting nanowires,²⁰ and carbon nanotubes.²¹ Given the low mass of the MEMS device and the electronically controlled actuation and load sensing, we conducted a combined experimental and multiphysics simulation study to assess the range of strain rates over which this MEMS device can be used for tensile testing of nanowires.

In order to achieve a constant strain rate, we designed a particular actuation voltage waveform, which can produce a constant velocity at the end of the specimen attached to the actuator shuttle (see SI Discussion S1). As a validation, this voltage waveform (based on SI eq S7) was applied to a MEMS device in which the gripping shuttles were epoxy-glued to each other, as shown in SI Figure S1. The resultant displacement of the thermal actuator was indeed measured to be linear as shown in SI Figure S2a.



Figure 3. Silver nanowire atomic structure obtained by means of electron microscopy. (a) TEM image showing the bicrystalline nature of the nanowire (scale bar is 3 nm). (b) HRTEM image showing the grain boundary along the nanowire axis (scale bar is 2 nm) (c) Indexed SAED image (scale bar is 2 nm⁻¹). (d) and (e) HRTEM images of the two single-crystal domains $[1\overline{1}1]$ and $[1\overline{1}0]$, respectively (scale bar is 1 nm). (f) Atomic model of the bicrystalline nanowire used in MD simulations.

Unlike previous work,⁶ where testing was conducted at quasistatic strain rates, using imaging to determine the nanowire strain is not possible for high strain rate tests. This limitation arises because the frame rate of image capture in commercial electron microscopes (\sim 35 frames/s) is insufficient for these dynamic experiments. In order to measure strain using imaging, at strain rates of 2/s over \sim 168 ms, it would require a frame rate of \sim 5000 frames/s to obtain sufficient data points for calculating the strain without significant errors.¹¹ Therefore, deformation of the specimen is obtained from electronic measurements by subtracting the calibrated thermal actuator displacement (which is a function of applied voltage) and the measured load sensor displacement. As a result, characterization of the displacement response of the thermal actuator under voltage waveforms of interest is required.

To identify the maximum actuation speed that the thermal actuator can impose on the nanowire, we conducted a series of experiments and COMSOL multiphysics electrothermomechanical analysis (see SI Discussion S1). Both the experiments and simulations showed that the thermal actuator displacement remains linear until 10 μ m/s, beyond this speed the thermal actuator starts to lag due to the inertia of the system. Therefore, in this study we limit the maximum speed used in the experiments to 10 μ m/s, which translates to a strain rate of 2/s for a nanowire gage length of approximately 3.5 μ m.

Case Study: Bicrystalline Silver Nanowires. The atomic structure of silver nanowires, purchased from Blue Nano Inc. and drop casted onto a Holey TEM grid, were characterized using TEM. Bright field high resolution TEM (HRTEM) and selected area electron diffraction (SAED) images of the nanowires as shown in Figure 3a and c respectively, revealed their bicrystalline nature. The diffraction patterns shown in Figure 3c are overlaps

of the $[1\overline{1}1]$ and $[1\overline{1}0]$ zone axes of the FCC crystal structure. The bicrystallinity is also evident from the different lattice fringes on either side of the wire, and the clear boundary between them. The interatomic spacing, measured from the diffraction pattern and HRTEM images, as seen in Figure 3c-e, were calculated to be 1.64 Å, 2.89 Å, and 4.01 Å, which correspond to the spacing of (112), (110), and (100), respectively.

On the basis of the measured crystallographic orientations, we built an atomic model of the nanowire to be used in MD simulations, as shown in Figure 3f. The projected atomic patterns for grains A and B, along the *x* direction (TEM zone axis), match the patterns shown in HRTEM images (Figure 3d and e). The two grains are tilted by 35.26° about the [110] direction. Moreover, the ratio of the lattice periodicities in the two grains, along the x direction, is an irrational number $(3)^{1/2}$: $((2)^{1/2}/2)$. Therefore, the bicrystal nanowire has a high-angle asymmetric irrational grain boundary (GB) structure as seen from Figure 3b. To model this GB, we employed a periodic approximation by taking the number of units of grain A and B along the *x* direction as 20 and 49, respectively, which requires a 0.01% strain to accommodate the mismatch inside the crystals. The diameter of the nanowire model used in the MD simulations is 14.17 nm and the length to diameter ratio is about 3. The details about the construction of the atomistic model are given in the SI Discussion S2.

Rate-Dependent Plasticity: Brittle to Ductile Transition. To characterize rate effects on nanowire deformation and failure, we measured the engineering stress–strain relationship at different strain rates in the range of 2×10^{-4} /s to 2/s. Representative curves are plotted in Figure 4 and a summary of parameters extracted from them including initial modulus, yield stress, and failure strain are given in SI Table S1. The modulus of



Figure 4. Stress-strain curves at different strain rates obtained from tensile test experiments (dashed lines are fits).

the bicrystalline silver nanowires, obtained from the quasistatic unloading from 1.5% strain, is 84.6 \pm 4.26 GPa, which is close to the bulk modulus for silver in the [110] direction.²² Up to a strain rate of 0.02/s, the nanowires fail in a brittle-like fashion. At higher strain rates, a drastic increase in ductility is observed, accompanied by strain hardening. The failure strain increases by 160% from 0.03 to 0.075 as the strain rate increases from 0.02/ s to 2/s. Figure 5 shows TEM images of the nanowires tested at various strain rates. All fracture surfaces reveal the evidence of necking before failure (fracture surfaces with high magnifications are shown in the insets). The stress drop beyond necking was not captured in the stress—strain curves shown in Figure 4 because the tensile experiments were conducted under load control.

It is important to note that the nanowires used in the experiments have surface undulations that arise from surface atomic steps resulting from the synthesis process, see SI Figure S3. As previously reported,¹⁷ the surface undulations create stress concentrations, such that the deformation may become unstable as the weakest cross section of the nanowire shrinks faster than the rest. When the strain rates are below 0.2/s, the nanowires

exhibit limited plastic straining as the deformation localizes in the necking region. This feature is more similar to the behavior observed in single-crystal metallic nanowires than to the one observed in penta-twinned nanowires. In the latter, a strong size scale-dependent plastic deformation and hardening was observed, ^{11,16,17} which was consistent with the accumulation of stacking fault decahedra as a result of the presence of internal twinned boundaries. In this low strain rate regime, TEM inspection of the bicrystal nanowires (Figure 5a and b) shows plastic deformation only in very few localized regions. By contrast, nanowires tested at high strain rates (above 0.2/s) show distributed plastic deformation along the entire nanowire (Figure 5c and d), which subsequently leads to strain hardening before the occurrence of necking (see Figure 5e for a higher magnification picture of a region showing a displaced grain boundary). The delay of necking and strain hardening above a threshold strain rate merits further analysis, which is provided in the following paragraphs and in the section on atomistic simulations.

According to Hart's theory,²³ strain rate-dependent materials become unstable in tension when

$$\frac{1}{\tau}\frac{\partial\tau}{\partial e} + m \le 1 \tag{1}$$

where τ and e are true stress and natural strain, respectively, and m is the strain rate sensitivity.²⁴ Equation 1 reduces to the classical Considère criterion²⁵ $((\partial \tau/\partial e) \leq \tau)$ for materials with negligible strain rate sensitivity. It reveals that the onset of necking could be suppressed by both strain hardening and strain rate sensitivity m. According to this criterion, the high yield stress (>1 GPa) of nanowires makes it easy for tensile instability to occur at small strains. In fact, it has been reported previously that single-crystal nanowires with diameter less than 100 nm fail in a brittle fashion.^{2,26} We calculate m from the slope of the logarithm of yield stress versus strain rate, as used in previous studies.^{2,3} To define the onset of yielding, we used the 0.2% strain offset except for the cases of brittle-like behavior (early necking), in which



Figure 5. Stitched TEM images of the bicrystalline nanowires tested at (a) quasistatic 0.003/s strain rate (scale bar -80 nm), (b) 0.02/s strain rate (scale bar -80 nm), (c) 0.2/s (scale bar -80 nm), and (d) 2/s (scale bar -100 nm). Red arrows point to plastic regions. Fracture surfaces with high magnifications are shown in the insets. Nanowires tested at higher strain rates show more plastic regions. (e) Representative region in the nanowire tested at high strain rate, where the dislocations have reacted with the grain boundary (GB). This shows that the contrast of plastic zones seen in the stitched TEM images are places where dislocations propagated and reacted with the GB leading to GB migration. Because the GB is not perfectly parallel to the electron beam, Moiré fringes of the GB are seen in these TEM images. (Scale bars: 4 and 2 nm, respectively.)

case, we used the maximum stress. These results are summarized in Figure 6, where the strain rate sensitivity *m*, for tests conducted



Figure 6. Yield stress at different strain rates. Circle points are from experiments (the data was averaged from multiple experiments conducted at the same strain rate; see SI Table S1); Square points are from MD simulation for nanowire with 42 nm length; the red curve is the prediction from dislocation nucleation theory for a nanowire with the same length as that used in experiments $(3.5 \,\mu\text{m})$.

below 0.02/s strain rate, was calculated as 0.086, which is greater than that for bulk silver (m = 0.005) at room temperature.²⁷ The calculated strain rate sensitivity is comparable to the values

reported for 75 nm diameter copper nanopillars (m = 0.11),³ and 100 nm diameter nickel nanowires (m = 0.098),² which were tested under similar strain rates in compression and tension, respectively. However, the value of *m* is still not sufficiently large to resist the inhomogeneous deformation at low strain rate when strain hardening is absent. Beyond a strain rate of ~0.2/*s*, we noticed that the yield stress becomes less sensitive to strain rate and the value of *m* drops from 0.086 to 0.037. Also, the nanowires fail in a ductile manner with increased plastic deformation, pointing to a delay in necking due to strain hardening. It should be noted that this rate-controlled brittle-to-ductile transition has not been reported earlier in literature due to the limited range of strain rates (<0.01/s) previously investigated. To understand the rate-controlling mechanism, we estimated the activation volume (Ω) from experiments using the following equation:

$$\Omega = k_{\rm B} T \frac{\partial \ln(\dot{\varepsilon})}{\partial \sigma} \tag{2}$$

By fitting the experimental data, we obtained the activation volumes of $1.00b^3$ and $1.82b^3$, respectively, for low (<0.2/s) and high strain rates ($\geq 0.2/s$), where *b* is the Burgers vector for a perfect dislocation in silver. Such small activation volumes suggest that the rate dependence in bicrystalline nanowires is controlled by dislocation nucleation.^{2,3,9,28,29} By comparison, bulk FCC metals generally have large activation volume (~100–



Figure 7. Snapshots from MD simulation at a strain rate of $10^6/s$, where only atoms with a centro-symmetry parameter greater than four are visualized. The following color convention is used: red plane, stacking fault; blue plane, twin plane; green line, Shockley partial; blue line, stair-rod dislocation; yellow line, Hirth partial. (a) and (b) Leading partial dislocation nucleation from the surface of the nanowire at 5.4% strain. (c) and (d) Slip and twinning in the nanowire at 7.8% strain, as well as the GB migration due to the dislocation/GB interaction and the stair-rod dislocation formed by partial dislocation reactions. In (a) and (c), a semitransparent mesh is constructed on nanowire surface for visualizing internal defects as well as surface morphology. In (d), only the surface mesh and dislocation lines are shown. Two types of twinning processes: (e) when a leading partial dislocation is nucleated on a plane right above an existing slip plane or (f) when a trailing partial dislocation is nucleated in the middle of a quad staking fault. The software OVITO³⁰ is used for visualization.

1000 b^3), where the plastic deformation is dominated by forest dislocation interactions.²⁴

Atomistic Investigation of Rate-Dependent Plasticity. To investigate rate sensitivity in the plastic deformation of bicrystalline silver nanowires, we carried out molecular dynamics simulations in uniaxial tension with the atomistic model shown in Figure 3f (see SI Discussion S3 for details of simulation). As in other FCC nanowires,^{16,17} plastic deformation is always found to begin by the nucleation of Shockley partial dislocations from the free surface. Stochastically, the nucleation could be initiated either from grain A or B. Figure 7a and b shows that a partial dislocation started from grain A and then swept the entire cross section of that grain, leaving an intrinsic stacking fault plane. One end of the dislocation escaped from the free surface, whereas the other one reacted with the GB. Due to the interaction between partial dislocation and GB, more partial dislocations were triggered from the GB, which propagate inside grain B. Moreover, because the two grains had different orientations, the asymmetric dislocation/GB interactions on the interface from both grains induce a GB migration along the length direction, as illustrated in Figure 7c. The HRTEM images obtained from a tested nanowire, Figure 5e, also confirm the atomistic signature associated with GB migration.

Slip and twinning are both observed in our MD simulation, which can be understood by considering the effect of Schmid factors.³¹ The possible slip planes in both grains are (111) and $(11\overline{1})$, on which the Schmid factors for the leading and trailing partial dislocation are, respectively, 0.471 and 0.236. When a leading partial dislocation is nucleated from the surface or GB, it is unlikely to be followed by a trailing partial dislocation; instead, more leading partial dislocations are nucleated on other slip planes, generating many parallel stacking fault planes. At the same time, twinning also occurs when a leading partial dislocation is nucleated on a plane right above an existing partial slip plane (Figure 7e), or when a trailing partial dislocation is nucleated in the middle of a quad stacking fault (Figure 7f). It is noted that when two partial dislocations glide on nonparallel planes and meet, they can react and form stair-rod dislocations that act as strong barriers to the gliding of further dislocations, as shown in Figure 7c and d. Apparently, the chance of forming these sessile dislocations increases at higher strain rates when dislocation density is higher, which could explain the significant strain hardening observed in the experiments conducted at high strain rates. In particular, these sessile dislocations can be formed inside both of the bicrystal grains, potentially making the strain hardening more prominent compared to single-crystal nanowires. In addition, GB can also provide strain hardening because partial dislocations can pile up and produce a back stress to oppose the applied stress on the slip plane.

We conducted MD simulations at three different strain rates $10^6/s$, $10^7/s$, and $10^8/s$. The deformation mechanism illustrated in Figure 7 remains the same at different strain rates, whereas the yield stress slightly decreases with decreasing strain rate, as shown in SI Figure S5. All the curves show a large stress drop right after yield, which is common in nanowire MD simulations.^{17,32,33} Such a stress drop is not seen in experiments which are performed under force control. We have previously observed stress drops followed by hardening in silver nanowires experimentally tested in tension under displacement control.¹⁶ Moreover, the atomistic model used in the MD simulations is for perfect nanowires. Also, all MD simulations indicate that the yield of nanowires starts with surface dislocation nucleation, as suggested by the small activation volume estimated from

experiments. It is noted that MD simulations predict higher yield stress (2.9-3.0 GPa) than experiments (1.56-2.62 GPa). The difference is related to the difference in strain rates between MD and experiments, although such a difference has been decreased to 6 orders of magnitude in the present study. In order to correlate MD simulation and experiments, we apply dislocation nucleation theory,^{8,9,34} in particular, we followed the approach used by Ryu, Kang, and Cai.⁸

According to the transition state theory,⁷ the dislocation nucleation rate, that is, the probability of dislocation nucleation per unit time, as a function of prescribed stress σ and temperature *T*, can be written as

$$v(\sigma, T) = Nv_0 \exp\left(-\frac{G_{\rm C}(\sigma, T)}{k_{\rm B}T}\right)$$
(3)

where $G_c(\sigma,T)$ is the activation Gibbs free energy for dislocation nucleation, *N* is the number of nucleation sites, v_0 is a frequency prefactor and k_B is the Boltzmann constant. On this basis, the most probable stress for dislocation nucleation (i.e., nucleation stress) at different strain rates can be found by solving the following equation:

$$\frac{G_{\rm c}(\sigma, T)}{k_{\rm B}T} = \ln \left\{ \frac{k_{\rm B}TNv_0}{\dot{\varepsilon}[\Omega_{\rm c}(\sigma, T)E_{\rm T}(\sigma, T) - k_{\rm B}T(\partial E_{\rm T}/\partial\sigma)]} \right\}$$
(4)

where $E_{\rm T}(\sigma)$ is the tangential modulus of nanowire. This equation is analogous to eq 2 in ref 9 derived by Zhu et al., except that here, we considered the stress-strain nonlinearity of bicrystalline nanowires as shown in SI Figure S5. A derivation of eq 4 is given in SI Discussion S5. The values of $G_c(\sigma,T)$ at different stress levels can be estimated based on energy barriers for dislocation nucleation.⁸ Using the climbed-image nudged elastic band (CINEB) method³⁵ and taking an initial state as a dislocation free nanowire and a final state with a full intrinsic stacking fault inside grain A, we can find the transition state and corresponding energy barrier for dislocation nucleation. Similar results are expected if the stacking fault is considered in grain B as both these grains are loaded on the same crystal direction ([110]) and the resultant shear stresses are equal on the same slip plane. Notably, transition state theory confirms dislocation nucleation from the nanowire surface. The details of energy barrier calculation are given in SI Discussion S4. As shown in Figure 8, $G_c(\sigma, T)$ decreases as stress increases, implying that the stress facilitates the thermally activated nucleation process.

The activation volumes, obtained as the derivative of G_c with respect to stress, are between 2 and $15b^3$, which are consistent with experiments and previously reported activation volumes of surface sources.^{2,3,36} In eq 4, the number of nucleation sites N can be estimated as $2(L/l_0)$, where *L* is the length of the nanowire, l_0 is the periodicity along the nanowire length and the factor of 2 is to account for the two grains. Using the length in MD simulation (L = 42 nm) and frequency prefactor $v_0 = 10^{-12}$, we numerically solved eq 4 and obtained the nucleation stress as a function of strain rate, which compares closely to MD simulations, as shown in SI Figure S8. Using the same frequency prefactor but the length of nanowire used in experiments ($L = 3.5 \ \mu m$), we can further calculate the nucleation stress at experimental strain rates and compare it to the yield stress measured experimentally, which is plotted in Figure 6 along with the experimental and MD data. Both theory and experiment show that yield stress increases with increasing strain rate, meaning a larger stress is required to gain a higher dislocation nucleation rate when the nanowire is



Figure 8. Activation Gibbs free energy of dislocation nucleation as a function of stress, fitted by a quadratic function. The insets show the initial and final states (red color indicates an intrinsic staking fault plane) used for CINEB calculations.

deformed more rapidly. It is noted that the yield stresses measured in high strain rate tests (0.2/s and 2/s), when the nanowire displays ductility, compare closely to nucleation theory predictions. On this basis, we hypothesize that the yield stress will continuously follow the nucleation theory when the strain rate is further increased.

Certainly, more experiments at higher strain rate (>2/s) need to be developed in the future to test this hypothesis. From examination of Figure 6, we also note that the yield stresses measured at low strain rates $(\langle 0.2/s \rangle)$ are considerably lower than those predicted by nucleation theory. This is likely due to the random surface imperfections, on the nanowire used in experiments (see SI Figure S3), which can trigger localized plasticity at these low strain rates. By contrast, surface nonuniformity was not considered in our numerical calculations. In fact, eq 4 was derived by assuming that all N possible nucleation sites in the nanowire have equal probability for dislocation nucleation. This assumption is true for pristine nanowire as used in MD simulations but not for the experimentally tested nanowires. HRTEM reveals that some surface sites are comparably weaker than others because of surface undulations (see SI Figure S3). It is hypothesized that dislocation nucleation occurs more easily on those weak sites at a stress lower than the theoretical predictions. Moreover, at low strain rates (<0.2/s), when plastic deformation starts at comparably lower stress levels, subsequent dislocation nucleation is preferable at places that are close to the initial nucleation. As such, plastic deformation develops only locally until necking, resulting in a brittle-like failure. By contrast, at higher strain rates $(\geq 0.2/s)$, as yield stress increases, the majority of surface sites become susceptible to dislocation nucleation beyond a sufficiently large stress, leading to distributed plastic deformation and hence pronounced ductility, observed experimentally (Figures 4 and 5). On the basis of the comparison between experiment and theory, Figure 6 shows that a brittle-to-ductile transition occurs when the stress approaches the one predicted by nucleation theory. In assessing the accuracy of this prediction, it should be kept in mind that the nanowire diameter used in MD and theoretical calculations is smaller than those used in the experiments. The values of yield stress in a larger diameter nanowire should be slightly smaller because dislocation nucleation becomes easier due to the reduced effect of the grain boundary strain field.

As noted in both experiment and MD simulation, the grain boundary in bicrystalline nanowire is essential for the strain hardening and pronounced plasticity at high strain rates, and thus, it plays an important role in brittle-to-ductile transition. For single-crystal nanowire without grain boundary, it has been reported previously that an increase of strain rate from 10^{-4} /s to 10^{-3} /s, on submicron tensile testing of single-crystal aluminum, results in a surge in dislocation density as the dislocation nucleation rate outweighs the loss rate.³⁷ This suggests the brittle-to-ductile transition observed in bicrystals may also be present in single crystals. Hence, it will be of interest for future work to examine rate-dependent behavior of single-crystal nanowires.

Conclusion. We have studied the strain rate-dependent plastic deformation of bicrystalline silver nanowires using both in situ electron microscopy experiments and atomistic simulations. By employing MEMS technology, deformations at speeds as high as $10 \,\mu\text{m/s}$ were investigated. By varying the experimental strain rate from 2×10^{-4} /s to 2/s, we observed a strong rate-dependent plastic behavior and found that bicrystalline silver nanowires fail in a brittle-like fashion (early strain localization) at low strain rates (<0.2/s). When the stain rate exceeds a threshold, a drastic increase in ductility with strain hardening was identified. This behavior is consistent with HRTEM images showing localized plastic deformation in brittle-fractured nanowires and more distributed plastic deformation in wires tested at higher rates.

MD simulations show that the initial nucleation of partial dislocation starts from the surface of the nanowire, leading to subsequent interaction between dislocations and GB and triggering GB migration and emission of further dislocations onto the other grain. When two dislocations glide on nonparallel planes inside the crystal, they form stair-rod dislocations that provide strain hardening. This feature is more prominent as the strain rate increases and the nucleation density increases.

Dislocation nucleation theory was employed to extrapolate the yield stress from MD simulations to the experimental strain rates. Nucleation theory predicted the yield stress to decrease with decreasing strain rates. The predicted yield stress values are in agreement with the experimental data for strain rates above 0.2/s when hardening and delay of necking takes place, that is, when the experimental mechanism is consistent with the MD predicted mechanism. At lower strain rates, random imperfections on the nanowire surface trigger localized plasticity with limited hardening, which promotes necking as predicted by Hart's theory. Indeed, because the yield stress at low strain tests (<0.2/ s) is comparably small, the subsequent nucleation and plastic deformation would be more likely to occur locally around the initial nucleation, resulting in a brittle-like failure. Thus, the brittle-to-ductile transition is found to occur when the yield stress approaches to the one predicted by nucleation theory.

The present study has reduced the strain rate gap between simulations and experiments from 11 to 6 orders of magnitude. Furthermore, it illustrates a pathway for the design of novel microsystems that when combined with advances in computational power should result in true one-to-one comparison between experiments and simulations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano-lett.5b03630.

Section S1 explains the experimental methodology of MEMS based tensile testing. Section S2 shows the details

of building atomistic model for bicrystalline nanowire. Section S3 provides the details of MD simulation method. Section S4 describes the method of energy barrier calculation. Section S5 explains the method of predicting nucleation stress. Table S1 summarizes the parameters extracted from the various strain rate tests. (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: espinosa@northwestern.edu.

Author Contributions

R.R. and W.G. contributed equally to this work.

R.R. performed the experiments. R.R., W.G., and R.B. analyzed the experiments. W.G. performed the atomistic simulations and theoretical analysis. H.E. conceived the research and provided guidance throughout the research. All the authors wrote the paper.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

H.D.E. gratefully acknowledges support from NSF through award No. DMR-1408901. This work made use of the EPIC facility (NUANCE Center-Northwestern University), which has received support from the MRSEC program (NSF DMR-1121262) at the Materials Research Center, and the Nanoscale Science and Engineering Center (EEC-0118025/003), both programs of the National Science Foundation; the State of Illinois; and Northwestern University. We thank Dr. Shuyou Li, Dr. Jinsong Wu, and Dr. Fengyuan Shi for help with TEM imaging. We also thank Dr. Penghao Xiao from University of Texas at Austin and Prof. Seunghwa Ryu from Korea Advanced Institute of Science and Technology for helpful discussions on atomistic modeling. This work used the Extreme Science and Engineering Discovery Environment (XSEDE)³⁸ under allocation TG-MSS140028, which is supported by National Science Foundation grant number ACI-1053575. The authors acknowledge the Texas Advanced Computing Center (TACC) at the University of Texas at Austin for providing HPC resources that have contributed to the research results reported within this paper.

REFERENCES

(1) Chen, L. Y.; He, M.-r.; Shin, J.; Richter, G.; Gianola, D. S. Measuring surface dislocation nucleation in defect-scarce nanostructures. *Nat. Mater.* **2015**, *14*, 707–713.

(2) Peng, C.; Zhong, Y.; Lu, Y.; Narayanan, S.; Zhu, T.; Lou, J. Strain rate dependent mechanical properties in single crystal nickel nanowires. *Appl. Phys. Lett.* **2013**, *102*, 083102.

(3) Jennings, A. T.; Li, J.; Greer, J. R. Emergence of strain-rate sensitivity in Cu nanopillars: Transition from dislocation multiplication to dislocation nucleation. *Acta Mater.* **2011**, *59*, 5627–5637.

(4) Greer, J. R.; De Hosson, J. T. M. Plasticity in small-sized metallic systems: Intrinsic versus extrinsic size effect. *Prog. Mater. Sci.* 2011, *56*, 654–724.

(5) Legros, M.; Gianola, D.; Motz, C. Quantitative in situ mechanical testing in electron microscopes. *MRS Bull.* **2010**, *35*, 354–360.

(6) Espinosa, H. D.; Zhu, Y.; Moldovan, N. Design and operation of a MEMS-based material testing system for nanomechanical characterization. J. Microelectromech. Syst. **2007**, *16*, 1219–1231.

(7) Hanggi, P.; Talkner, P.; Borkovec, M. Reaction-Rate Theory - 50 Years after Kramers. *Rev. Mod. Phys.* **1990**, *62*, 251–341.

(8) Ryu, S.; Kang, K.; Cai, W. Predicting the dislocation nucleation rate as a function of temperature and stress. *J. Mater. Res.* **2011**, *26*, 2335–2354.

(9) Zhu, T.; Li, J.; Samanta, A.; Leach, A.; Gall, K. Temperature and strain-rate dependence of surface dislocation nucleation. *Phys. Rev. Lett.* **2008**, *100*, 025502.

(10) Deng, C.; Sansoz, F. Fundamental differences in the plasticity of periodically twinned nanowires in Au, Ag, Al, Cu, Pb and Ni. *Acta Mater.* **2009**, *57*, 6090–6101.

(11) Ramachandramoorthy, R.; Bernal, R.; Espinosa, H. D. Pushing the Envelope of In Situ Transmission Electron Microscopy. *ACS Nano* **2015**, *9*, 4675–4685.

(12) Hu, L.; Kim, H. S.; Lee, J.-Y.; Peumans, P.; Cui, Y. Scalable coating and properties of transparent, flexible, silver nanowire electrodes. *ACS Nano* **2010**, *4*, 2955–2963.

(13) Wiley, B.; Sun, Y.; Xia, Y. Synthesis of silver nanostructures with controlled shapes and properties. *Acc. Chem. Res.* **2007**, *40*, 1067–1076.

(14) Narayanan, S.; Cheng, G. M.; Zeng, Z.; Zhu, Y.; Zhu, T. Strain Hardening and Size Effect in Five-fold Twinned Ag Nanowires. *Nano Lett.* **2015**, *15*, 4037–4044.

(15) Qin, Q. Q.; Yin, S.; Cheng, G. M.; Li, X. Y.; Chang, T. H.; Richter, G.; Zhu, Y.; Gao, H. J. Recoverable plasticity in penta-twinned metallic nanowires governed by dislocation nucleation and retraction. *Nat. Commun.* **2015**, *6*, 5983.

(16) Bernal, R. A.; Aghaei, A.; Lee, S.; Ryu, S.; Sohn, K. N.; Huang, J.; Cai, W.; Espinosa, H. D. Intrinsic Bauschinger Effect and Recoverable Plasticity in Penta-twinned Silver Nanowires Tested in Tension. *Nano Lett.* **2015**, *15*, 139–146.

(17) Filleter, T.; Ryu, S.; Kang, K.; Yin, J.; Bernal, R. A.; Sohn, K.; Li, S. Y.; Huang, J. X.; Cai, W.; Espinosa, H. D. Nucleation-Controlled Distributed Plasticity in Penta-twinned Silver Nanowires. *Small* **2012**, *8*, 2986–2993.

(18) Zhu, Y.; Espinosa, H. D. An electromechanical material testing system for in situ electron microscopy and applications. *Proc. Natl. Acad. Sci. U. S. A.* **2005**, *102*, 14503–14508.

(19) Pantano, M. F.; Bernal, R. A.; Pagnotta, L.; Espinosa, H. D. Multiphysics design and implementation of a microsystem for displacement-controlled tensile testing of nanomaterials. *Meccanica* **2015**, *50*, 549–560.

(20) Agrawal, R.; Peng, B.; Espinosa, H. D. Experimental-computational investigation of ZnO nanowires strength and fracture. *Nano Lett.* **2009**, *9*, 4177–4183.

(21) Peng, B.; Locascio, M.; Zapol, P.; Li, S.; Mielke, S. L.; Schatz, G. C.; Espinosa, H. D. Measurements of near-ultimate strength for multiwalled carbon nanotubes and irradiation-induced crosslinking improvements. *Nat. Nanotechnol.* **2008**, *3*, 626–631.

(22) Courtney, T. H. *Mechanical behavior of materials;* Waveland Press: Long Grove, IL, 2005.

(23) Hart, E. W. Theory of Tensile Test. *Acta Metall.* **1967**, *15*, 351–355.

(24) Dieter, G. E.; Bacon, D. Mechanical metallurgy; McGraw-Hill: New York, 1986; Vol. 3.

(25) Considère, A. Ann. Ponts Chaussées 1885, 9, 574-775.

(26) Richter, G.; Hillerich, K.; Gianola, D. S.; Monig, R.; Kraft, O.; Volkert, C. A. Ultrahigh Strength Single Crystalline Nanowhiskers

Grown by Physical Vapor Deposition. *Nano Lett.* **2009**, *9*, 3048–3052. (27) Kassner, M. The rate dependence and microstructure of highpurity silver deformed to large strains between 0.16 and 0.30 T m. *Metall. Trans. A* **1989**, *20*, 2001–2010.

(28) Li, J. The mechanics and physics of defect nucleation. *MRS Bull.* **2007**, 32, 151–159.

(29) Zhu, T.; Li, J. Ultra-strength materials. Prog. Mater. Sci. 2010, 55, 710–757.

(30) Stukowski, A. Visualization and analysis of atomistic simulation data with OVITO-the Open Visualization Tool. *Modell. Simul. Mater. Sci. Eng.* **2010**, *18*, 015012.

(31) Weinberger, C. R.; Cai, W. Plasticity of metal nanowires. J. Mater. Chem. 2012, 22, 3277–3292.

Letter

(32) Kheradmand, N.; Vehoff, H.; Barnoush, A. An insight into the role of the grain boundary in plastic deformation by means of a bicrystalline pillar compression test and atomistic simulation. *Acta Mater.* **2013**, *61*, 7454–7465.

(33) Tucker, G. J.; Aitken, Z. H.; Greer, J. R.; Weinberger, C. R. The mechanical behavior and deformation of bicrystalline nanowires. *Modell. Simul. Mater. Sci. Eng.* **2013**, *21*, 015004.

(34) Weinberger, C. R.; Jennings, A. T.; Kang, K.; Greer, J. R. Atomistic simulations and continuum modeling of dislocation nucleation and strength in gold nanowires. *J. Mech. Phys. Solids* **2012**, *60*, 84–103.

(35) Henkelman, G.; Uberuaga, B. P.; Jonsson, H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. J. Chem. Phys. **2000**, 113, 9901–9904.

(36) Zhu, T.; Li, J.; Samanta, A.; Kim, H. G.; Suresh, S. Interfacial plasticity governs strain rate sensitivity and ductility in nanostructured metals. *Proc. Natl. Acad. Sci. U. S. A.* **2007**, *104*, 3031–3036.

(37) Oh, S. H.; Legros, M.; Kiener, D.; Dehm, G. In situ observation of dislocation nucleation and escape in a submicrometre aluminium single crystal. *Nat. Mater.* **2009**, *8*, 95–100.

(38) Towns, J.; Cockerill, T.; Dahan, M.; Foster, I.; Gaither, K.; Grimshaw, A.; Hazlewood, V.; Lathrop, S.; Lifka, D.; Peterson, G. D.; Roskies, R.; Scott, J. R.; Wilkens-Diehr, N. XSEDE: Accelerating Scientific Discovery. *Comput. Sci. Eng.* **2014**, *16*, 62–74.