Quantifying the defect-dominated size effect of fracture strain in single crystalline ZnO nanowires

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The diameter (D) dependence of fracture strains in [0001]-oriented single crystalline ZnO nanowires (NWs) with D ranging from 18 to 114 nm is experimentally revealed via in situ uniaxial tension and is well understood based on an analytical model developed by combining molecular dynamics simulations with fracture mechanics theories. We show that the scattered fracture strains are dominated by the effective quantities of atomic vacancies, and their lower bound follows a power-form scaling law, resembling the Griffith-type behavior of single critical defects with diameter-dependent sizes, when D is larger than a critical Dc. In addition, theoretical strength is expected in NWs with D < Dc. Our studies provide a simple, but basic, understanding for the size effect of strengths in single crystalline NWs. © 2011 American Institute of Physics. [doi:10.1063/1.3594655]

I. INTRODUCTION

Strength is a basic mechanical property for both structural and functional materials. In macroscopic specimens, the fracture strength (σFS) is typically lower than 0.1% of the Young’s modulus (YM) and is dominated by a large amount of critical defects, the size distribution of which leads to the intrinsic scattering of σFS. As depicted by the Weibull statistics, the expected σFS of specimens increase as their characteristic sizes decrease, a condition known as size effect, which has been the core issue of fracture mechanics since Griffith.1

Recently, increasing attention paid to the mechanical properties in nanowires (NWs)3–8 and nanotubes (NTs)9–11 is extending the size effect into the nanoscale. Although the defect-dominated σFS in NTs have been well understood based on Griffith’s theory10 and atomistic simulations,11 for NWs, there were merely some preliminary experimental results on the size effect of σFS. For instance, Wen et al. reported a linear relationship between σFS and diameter (D) in ZnO NWs,3 Zhu et al. suggested that the σFS in Si NWs depended log-linearly on the surface areas,8 and Agrawal et al. attributed the σFS in ZnO NWs—which slightly decreased with increasing surface area—to the defects near the NW surfaces, based on Weibull statistical analysis and molecular dynamics (MD) simulations.5 However, the quantitative mechanisms for the size effect (i.e., how the scattered σFS are related to the NW diameters and, especially, how they are determined by the real microstructural defects in NWs) have not been theoretically clarified yet, but they are of basic importance for the potential application of NWs in nanoelectromechanical devices with predictable and reproducible responses.12

In our previous experiments,13 methodologies were developed for in situ uniaxial tensile testing using a scanning electron microscope (SEM). The diameter dependence of σFS has also been revealed in a concise form.14 Herein, we report detailed theoretical studies on the size effect of fracture strains (εFS), which is related to the quantities of native point defects as well as to the critical defect sizes in Griffith’s theory. An analytical scaling law is finally derived.

II. RESULTS AND DISCUSSIONS

Similar to σFS, εFS in single crystalline ZnO NWs with D ranging from 18 to 114 nm were measured via in situ SEM. The experimental details can be found elsewhere;13 in short, each individual NW was axially aligned with the tensile direction and was loaded by deflecting a cantilever [see Fig. 1(a)]. Based on a series of SEM images, the stress-strain (σ-ε) curve was calculated [see Fig. 1(b)].

The diameter dependence of εFS was then revealed [Fig. 1(c)]. We hereinafter focused on εFS instead of on the conventionally discussed σFS, seeing that the measurement error in the strain is smaller than that in the stress;15 moreover, the ideal strain (εth, i.e., the εFS in defect-free ZnO NWs) is more insensitive to D than is the ideal strength (σth), which means that the size effect of σFS is partly contributed by the surface-dominated diameter dependence of YM,13 whereas that of εFS is mostly defect-dominated.15 The remarkable scattering of εFS can thus be attributed to the size distribution of critical defects, and their size effect results from the reduction of critical defects with decreasing D, which is in accordance with previous qualitative reports.3–8

Concerning critical defects, Weibull statistical analysis is promising for revealing their size and spatial distribution.
in specimens. For NWs, it was conventionally assumed that for a mass of critical defects uniformly distributed on side surfaces, the probability of fracture (Pf) under a strain ($\varepsilon$) was related to the dimensionless surface area ($S$):

$$P_f(\varepsilon_{FS} < \varepsilon) = \frac{1}{C_0} \exp\left[-S \left(\frac{\varepsilon}{\varepsilon_0}\right)^m\right].$$  \hspace{1cm} (1a)

Here, $\varepsilon_0$ and $m$ depict the expected value and dispersion of $\varepsilon_{FS}$, respectively, for specimens with a unit $S$. Alternatively, a modified statistics was recently proposed for NTs having few (e.g., only one) critical defects, where $P_f$ and the expected strength $\varepsilon_0$ were no longer related to specimen sizes:

$$P_f(\varepsilon_{FS} < \varepsilon) = \frac{1}{C_0} \exp\left[-\left(\frac{\varepsilon}{\varepsilon_0}\right)^m\right].$$  \hspace{1cm} (1b)

As can be seen in Fig. 2, our experimental data were fitted unexpectedly well using Eq. (1b), yielding a correlation factor ($R^2$) close to 1, as were the values of $\varepsilon_{FS}$ in ZnO NWs measured via in situ free-end bending. In addition, the transverse intercept of the fitting curve was larger for bending ($\varepsilon_0 = 0.058$) than for tension ($\varepsilon_0 = 0.043$), manifesting the effect of the loading mode that has been well understood in bulk specimens.

In contrast, the conventional size-dependent statistics [Eq. (1a)] cannot work so satisfactorily. Therefore, the real microstructural defects in the tested NWs should behave as single critical defects, and the effect of surface defects can be ruled out. This knowledge from Weibull statistical analysis also agrees well with the key assumption that our tested ZnO NWs are free of planar defects and evident surface flaws.

On the other hand, our recent in situ cathodoluminescence experiments convincingly related the size effect of strength with the quantities of native point defects in NWs, which seems counterintuitive seeing that a single atomic vacancy, even located on the NW surfaces, cannot degrade $\varepsilon_{FS}$ to less than 80% of $\varepsilon_{th}$, while such a value is still far larger than most of our experimental data. Hence, MD simulations were carried out, aimed at finding the “combination effects” of discrete point defects.

The uniaxial tensile loading of bulk ZnO and [0001]-oriented NWs were modeled using the Large-scale Atomic/Molecular Massively Parallel Simulator. The supercell for pristine bulk ZnO was generated by repeating the wurtzite unit cell [see Fig. 3(a)] by 4, 6, and 12 units along the $\frac{1}{2}\frac{2}{1}\frac{1}{10}$, $\frac{1}{2}\frac{0}{1}\frac{1}{10}$, and [0001] axes, respectively, and periodic boundary conditions were applied in these three directions. The supercell for a NW with $D = 3.6$ nm and a length of 9.4 nm is shown in Fig. 3(a). The short-range atomic interactions were
described by a Buckingham-type potential, and the Coulomb interactions were calculated via Wolf summation. The initial relaxation, quasistatic loading, and calculation of $\sigma$-$\varepsilon$ curves were then performed according to our previous work. As Fig. 3(b) shows, a phase transformation from wurtzite to a body-centered-tetragonal lattice is predicted as before at points “A”. However, such post-elastic behaviors have actually not been observed yet during the in situ tensile testing of individual ZnO NWs, probably because that displacement-controlled tensile loading has not been realized in the nanoscale. As a result, the stress drop accompanied by the phase transformation can immediately fracture ZnO NWs that are intrinsically brittle materials. We also noted a recent first-principle calculation that suggested that the phase transformation cannot happen until the pristine NW fractured with an $\varepsilon_{\text{fr}}$, as high as 20%. Concerning the effect of defects on strength, however, no difference has been provided in comparison to MD simulations. Overall, it is yet reasonable to define the $\varepsilon_{\text{FS}}$, in our current MD studies, based on points “A”.

Then, the effect of point defects on $\varepsilon_{\text{FS}}$ was simulated by intentionally introducing vacancy-pairs (VPs) one by one into the supercell. Each time, a random $Q^{2-}$ site and one of its nearest-neighbor Zn$^{2+}$ site were simultaneously replaced by vacancies, in order to preserve the charge equilibrium. For the randomly introduced VPs, Fig. 3(c) reveals that $\varepsilon_{\text{FS}}$ (in both the bulk and the NWs) decreased as the quantity ($Q$) of VPs increased. Moreover, a range of $\varepsilon_{\text{FS}}$ can be obtained for a given $Q$ (take $Q = 1$ and 2, for example). As revealed in Fig. 3(d), $\varepsilon_{\text{FS}}$ can be degraded more remarkably when the two VPs are aligned parallel to the [0001] cleavage plane, which does suggest some interactions between discrete point defects, such as stress concentrations and defect aggregations via atomic diffusions.

After all, $\varepsilon_{\text{FS}}$ not only depended on the quantity of point defects, but also were affected by the spatial configuration of these VPs; we can thus define the effective sizes ($n$) of the single critical defects, which uniquely determine $\varepsilon_{\text{FS}}$, as

$$n^2 = \eta Q.$$  

Here, $n$ is normalized by the in-plane lattice constant. For each specific NW with a total of $Q$ VPs, $\eta$ depicts the proportion of the VPs involved in the above-suggested interactions, as well as the overall effects of the spatial configurations of these “active” defects. As indicated by Fig. 3(d), the upper bound of $n$ (simply let $\eta = 1$) corresponds to a sharp planar crack perpendicular to the [0001] NW axis, the fracture mechanics model for which can be analytically derived as

$$\varepsilon_{\text{FS}}(n) = \varepsilon_{\text{fr}}(1 + n)^{-\beta},$$  

based on an atomic-scale, i.e., “quantized” Griffith’s theory that has been widely applied to the $\sigma_{\text{FS}}$ in NTs. Nonetheless, Eq. (3) should generally work for $n$, because the geometric effect of the crack-tip radius can be included in the factor $\eta$.

First, Eq. (2) was confirmed by fitting the MD-simulated $\varepsilon_{\text{FS}}(Q)$ relationships using Eq. (3). A constant $\eta_{\text{average}}$ was supposed to calculate $n$ for the randomly introduced VPs. As seen in Fig. 3(c), the power factors $\beta = 0.21$ and 0.72 were yielded for the bulk and the NW ($D = 3.6$ nm), respectively, implying that $\varepsilon_{\text{FS}}$ in NWs is more sensitive to $Q$ than that in the bulk, because the point defects near free surfaces can lead to more intense stress concentrations than those in bulk materials.

The diameter dependence of $n(D)$ in the experimentally tested ZnO NWs was then determined by applying Eq. (3) to the $\varepsilon_{\text{FS}}(D)$ as measured in Fig. 1(c), where $D$ ranged from 18 to 114 nm. A classic $\beta = 0.50$ representing the Griffith’s
scaling law was utilized as a reasonable simplification, and \( \epsilon_{\text{th}} \) was assumed to be the constant \( \sim 0.09 \) that was simulated in bulk ZnO. \(^{15}\) Straightforwardly, the scattering of experimental \( n(D) \) for a given \( D \) (see Fig. 4) resulted from the stochastic and specimen-specific factor \( \eta \); moreover, the diameter-dependent upper bound of \( n(D) \) can be simply modeled by assuming \( \eta = 1 \), which means that all of the native point defects in NWs are “active” in dominating their minimum strengths. As a result, one has \( n_{\text{max}}^2(D) = Q(D) = \lambda D^2C(D) \), where \( \lambda \) is the length scale depicting the interactions between point defects, and the concentration of point defects \( C(D) = C_0 \exp(-\Delta p \bar{\Omega}k_b T) \). Here, \( C_0 \) is the concentration in bulk materials, \( \bar{\Omega} \) is the volume of the Zn\(^{2+} \) and O\(^{2-} \) vacancies, \( k_b T \) is the Boltzmann factor, and \( \Delta p = 2 \eta / D \) (\( \tau \) is the surface tension in \{10\(\bar{1}\)0\} side surfaces). \(^{14}\) The size-dependent reduction of critical defect sizes thus can be derived as

\[
n_{\text{max}}(D) = \sqrt{\lambda C_0 D} \exp\left(-\frac{\tau \bar{\Omega}}{k_b T} \right) \approx \alpha \max(D - D_c, 0),
\]

where \( \alpha \) is a constant. Hence, a critical NW diameter was derived as \( D_c = \frac{\tau \bar{\Omega}}{k_b T} \), concerning the ZnO NWs in experiments, and Eq. (4) predicted that critical defects no longer existed in NWs with \( D < D_c \); in other words, the strength became insensitive to defects. Similar behavior has been proposed in nano-laminated composites with \( D_c \) around 100 nm, \(^{25}\) but not yet in single crystalline NWs.

As Fig. 4 shows, fitting the experimental upper bound of \( n(D) \) using Eq. (4) yielded a good linear correlation; moreover, extrapolating the fitting curve to \( n_{\text{max}} = 0 \) yielded \( D_c = 11.6 \) nm, which agreed quantitatively well with \( \tau \bar{\Omega} / k_b T = 10.8 \) nm, where the surface tension in \{10\(\bar{1}\)0\} is estimated as \( \tau \sim 3.4 \) N/m. \(^{26}\) The ionic radii of O\(^{2-} \) and Zn\(^{2+} \) are 1.40 Å and 0.74 Å, respectively, and we assume \( T = 300 \) K. Therefore, the Griffith-type fracture mechanics for the effective \( n(D) \) of the single critical defects, which is defined as Eq. (2), was experimentally supported.

We finally return to the size effect of \( \epsilon_{\text{FS}} \). As seen in Fig. 1, the upper-bound of \( \epsilon_{\text{FS}} \) increased with decreasing \( D \), following a linear relationship that has nonetheless not been quantitatively modeled yet, as further probing into the fracture mechanism is still needed in order to find whether the minimum of the “active” defects \( (\eta Q) \) is random or diameter-dependent; while for the lower-bound of \( \epsilon_{\text{FS}} \), the following power law for \( D > D_c \) can be obtained by combining Eqs. (3) and (4):

\[
\epsilon_{\text{FS}}^\text{min}(D) = \epsilon_{\text{th}}[1 + \alpha(D - D_c)]^{-\beta} \quad \text{for } D > D_c
\]

Fitting the experimental \( \epsilon_{\text{FS}}(D) \) with Eq. (5) yielded \( \epsilon_{\text{th}} = 0.11 \) and \( \beta = 0.52 \) [see Fig. 1(c)], agreeing qualitatively with Griffith’s classic theories where \( \epsilon_{\text{th}} \sim 0.1 \) and \( \beta \sim 0.5 \). \(^{1,10}\) Ultimately, a modified power-form scaling law for the size effect of strengths was analytically derived, and we concluded, for the first time, that the classic fracture mechanics theories also work well for single crystalline NWs, as long as the effective quantities of point defects are regarded as critical defects.

III. CONCLUSIONS

In summary, the diameter dependence of \( \epsilon_{\text{FS}} \) in single crystalline ZnO NWs is experimentally revealed via in situ uniaxial tension and analytically modeled based on fracture mechanics theories and MD simulations. The scattered \( \epsilon_{\text{FS}} \) are dominated by the effective quantities of atomic vacancies, and the lower bound of \( \epsilon_{\text{FS}} \) follows a power law, resembling the Griffith-type behavior of single critical defects with diameter-dependent sizes. In addition, the theoretical strength is predicted in NWs with \( D < D_c \) (around 12 nm). Our studies account for a very simple case of single crystalline NWs; however, this should be the basis for fully understanding the size effect of strengths in the nanoscale.

We still need to state that the detailed mechanisms of fracture remain unclear, since it is challenging yet to (i) directly inspect the atomic-scale behaviors of point defects using in situ TEM and (ii) measure the post-elastic \( \sigma - \epsilon \) responses via displacement-controlled tensile experiments. More attention should be paid to experimental improvements in order to understand and ultimately control the strength properties in nanomaterials.

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