Large-Scale Density Functional Theory Investigation of Failure Modes in ZnO Nanowires

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ABSTRACT Electromechanical and photonic properties of semiconducting nanowires depend on their strain states and are limited by their extent of deformation. A fundamental understanding of the mechanical response of individual nanowires is therefore essential to assess system reliability and to define the design space of future nanowire-based devices. Here we perform a large-scale density functional theory (DFT) investigation of failure modes in zinc oxide (ZnO) nanowires. Nanowires as large as 3.6 nm in diameter with 864 atoms were investigated. The study reveals that pristine nanowires can be elastically deformed to strains as high as 20%, prior to a phase transition leading to fracture. The current study suggests that the phase transition predicted at ~10% strain in pristine nanowires by the Buckingham pairwise potential (BP) is an artifact of approximations inherent in the BP. Instead, DFT-based energy barrier calculations suggest that defects may trigger heterogeneous phase transition leading to failure. Thus, the difference previously reported between in situ electron microscopy tensile experiments (brittle fracture) and atomistic simulations (phase transition and secondary loading) (Agrawal, R.; Peng, B.; Espinosa, H. D. *Nano Lett.* **2009**, *9* (12), 4177–2183) is elucidated.

KEYWORDS Failure modes, zinc oxide, nanowires, density functional theory, phase transformation

emiconducting nanowires (NWs) with a nonsymmetric crystal structure have recently drawn significant research interest¹ because of their optoelectronic properties² and electromechanical coupling. For example, materials like zinc oxide (ZnO) and gallium nitride exhibit piezoelectricity,³⁻⁵ which provides a means of converting mechanical energy to electrical energy and vice versa. This electromechanical coupling combined with the fact that these materials are semiconducting has been exploited in the development of prototypes of energy harvesting devices.^{3,6,7} Mechanical energy associated with everyday life, like biomechanical motion,⁷ can thus be harnessed to produce enough electrical energy to drive portable electronic/medical devices that require small amounts of power.⁸ To address the reliability of such selfpowered nanowire-based devices, it is critical to develop an understanding of their failure modes.

Various experimental techniques have been used to investigate NW mechanical behavior. They include dynamic resonance in situ scanning electron microscopy,^{9,10} three-point bending experiments using atomic force microscopy (AFM),^{11–13} contact resonance AFM,¹⁴ nanoindentation,¹² and microfabricated loading stages-based^{15,16} and micro-electromechanical systems (MEMS)-based testing.¹⁷ In each technique, a different set of assumptions is used in the data interpretation. Even though discrepancies in elastic response

have been addressed,¹⁷ differences between experimentally and computationally reported failure mechanisms of ZnO NWs require further investigation. All the experimental studies report brittle failure at strains ranging from 3 to 6%.^{1,11,18} The variation in these strains is generally attributed to differences in intrinsic surface defects that arise during NW growth, as the wires are grown using a variety of methods.^{1,19,20}

This experimental picture stands in contrast to the results of atomic-scale molecular dynamics simulations using a Buckingham-type pairwise potential (MD-BP). In earlier MD-BP studies, the nanowires were uniaxially deformed along the c-axis at 300 K by applying displacements at the two ends of the nanowire with periodic boundary conditions. MD-BP predicts a stress-induced phase transition from the original wurtzite (WZ) phase to a body-centered tetragonal (BCT) phase at strains much smaller than those at which failure is predicted computationally.^{1,21,22} Such behavior has also been observed when surface defects were included, suggesting that defects do not inhibit transition initiation.¹ On the contrary, the presence of surface defects leads to heterogeneous nucleation of the phase transition accompanied by a reduction in the required average critical stress. However, as the existence of the transformed BCT phase has not been realized experimentally, a more thorough investigation seems appropriate to ensure that the behavior predicted by the BP (used in refs 1 and 17) is not an artifact of approximations inherent to BP.

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In ref 22, the transition observed in MD-BP simulations was justified based on density functional theory (DFT) calculation involving bulk crystals. In this study, unit cells with WZ and BCT crystal structures were modeled with PBCs in all the directions (to model bulk behavior) and their enthalpies were computed as a function of stress applied along [0001] direction. The authors of this study found that above a critical stress, the enthalpy of the BCT phase was lower than that of the WZ phase. This result seemed to confirm the possibility of the transition. However, this study had two important limitations: (i) NWs were not modeled, so it remains unclear what effect free surface might have; and (ii) energy barriers were not computed, so no estimate is available regarding the energy required to initiate the transition. In this paper, we address these limitations by performing an extensive DFT study of NWs ranging from 1.0 to 3.6 nm in diameter, which includes a careful analysis of the transition barrier. Comparisons are made between the DFT predictions and results obtained using molecular mechanics simulations based on a Buckingham-type potential (MM-BP), viz.

$$E_{\text{total}}(r_{ij}) = \sum_{i=1}^{N} \sum_{j \neq i} A \exp\left(-\frac{r_{ij}}{\rho}\right) - \frac{C}{r_{ij}^{6}} + E_{\text{long}}(r_{ij}) \quad (1)$$

where r_{ij} is the distance between atoms *i* and *j*. Parameters *A*, *C*, and ρ define the short-range interactions and were identified by Binks.²³ E_{long} represents the long-range Coulombic interactions, which were computed based on Wolf's summation technique.^{24,25} MM simulations at 0 K and not MD simulations were performed to facilitate a direct comparison to the DFT results. The large-scale atomic/molecular massively parallel simulator (LAMMPS) computer program developed at Sandia National Laboratories²⁶ was used for the MM simulations. A quasi-static loading scheme was used, in which a NW was deformed to a given strain, and then its geometry was optimized by way of energy minimized. This protocol was incrementally followed to strains beyond 20%. Further MM simulation procedure details can be found elsewhere.¹⁷

DFT calculations were performed using the SIESTA package.^{27,28} The generalized gradient approximation (GGA) was employed with Perdew–Burke–Ernzerhof (PBE)²⁹ and revised Perdew–Burke–Ernzerhof (RPBE)³⁰ functionals, and a double- ζ plus polarization orbital (DZP) basis set. The PBE functional has been shown to be a good general-purpose functional for solids.³¹ The RPBE functional has been reported to predict more accurate binding energies than PBE,³⁰ thus a comparative study was conducted to analyze the effect of the different functionals on the fracture properties. Pseudopotentials for Zn and O were generated using the Troullier–Martins scheme³² and are available via the SIESTA homepage.³³ Periodic boundary conditions were

TABLE 1. Residual Axial Stresses Computed As a Function of MP Grids and Unit Cell Lengths

MP Grid	length (c)	no. of atoms	residual Stress (GPa)
$1 \times 1 \times 1$	1 C	48	+10.06
$1 \times 1 \times 5$	1 C	48	-3.17
$1 \times 1 \times 9$	1 C	48	-3.17
$3 \times 3 \times 5$	1 C	48	-3.17
$1 \times 1 \times 1$	2c	96	-2.96
$1 \times 1 \times 1$	3c	144	-3.17
$1 \times 1 \times 1$	4c	192	-3.17

applied along the length of the nanowire and are necessary to avoid unrealistic wire-end effects. Bulk ZnO was used for model verification. The lattice parameters for bulk WZ ZnO were found using PBE/DZP to be a = 3.25 Å and c = 5.31 Å, which are in good agreement with values reported in the literature.³⁴

A convergence study was conducted using 1.0 nm NWs to determine an appropriate k-space mesh-point density. A NW of length 1*c* with different Monkhorst-Pack (MP) grids was used in a series of tests, the MP grid defining the mesh-point density. Grid dimensions of 1 × 1 × 1 (Γ -point calculation), 1 × 1 × 5, 1 × 1 × 9, and 3 × 3 × 5 along the NW axis were modeled.

The density of k-space mesh points is proportional to the size of the unit cell. Therefore, an increase in the density of points in k-space in, for example, the axial direction, can be achieved by increasing the size of the unit cell in that dimension. Although this increases the computational cost at a substantially higher rate than simply increasing the density of the mesh, it provides increased flexibility in atomic configurations. This is the case because it increases the distance between any given atom and its images in neighboring virtual unit cells along the axial direction. With this as motivation, the unit cell size was increased in the axial direction to 2c, 3c, and 4c for a second series of tests. In these cases, only the Γ -point was used to sample the (smaller) Brillouin zone. Table 1 summarizes the convergence test results. The residual stress in the z- (axial-) direction with the atoms arranged as they are in the bulk at their optimized geometry, was used as the measure for determining what constitutes a sufficiently fine mesh. These results indicate that using just the Γ -point in 1*c* calculations is insufficient. The predicted residual stress is not only incorrect in magnitude but also in sign. The 1c models with $1 \times 1 \times 5$ and $1 \times 1 \times 9$ MP grids are sufficient for the precise calculation of this stress, as are 3c and $4c \Gamma$ -point calculations. The 2c 1 \times 1 \times 1 mesh result is reasonably close to the converged value.

This investigation called for simulations with as wide a range of NW diameters as possible. Also, wires with diameters that are below a certain threshold lack any region that one could reasonably describe as a core. Therefore, nanowires with diameters of 1.0, 2.4, and 3.6 nm were modeled, which satisfy these requirements. The 2c wires with these diameters consist of 96, 384, and 864 atoms, respectively.

NANO LETTERS



FIGURE 1. Model of the 2.4 nm diameter ZnO NW (with 384 atoms) studied using DFT and MM-BP. (a) Cross-sectional view; (b) side view showing the length and the loading direction (green = zinc; yellow = oxygen). PBC stands for periodic boundary conditions.

Doing geometry optimizations with 864 atoms using just the Γ -point in PBE/DZP or RPBE/DZP calculations is a daunting task. An optimization at a single strain can take more than 14 000 (~110 × 128 processors) CPU hours.³⁵ Thus, to keep computer run times manageable and to obtain comparable results for all NW diameters, a cell length of 2*c* and an MP grid of 1 × 1 × 1 were used to model all the tensile tests reported hereafter. The 2.4 nm wire is shown in Figure 1.

The unit cell was incrementally strained to mimic displacement-controlled loading, and the atomic structures were geometry-optimized at each strain step to obtain the energy and axial stress at that strain. The results are reported in the following order. First, we discuss the effect of unrestricting the electron-spin using RPBE/DZP for a 1.0 nm NW. Second, we compare the mechanical behavior of 2.4 and 3.6 nm nanowires, as predicted by MM-BP and PBE/DZP. Third, the effect of wire diameter and the effect of different functional (PBE/DZP vs RPBE/DZP) on mechanical response are discussed. Finally, the energy barriers to phase transition are reported and results are discussed in the context of experimental measurements.

In density functional theory, requiring the electron spin of a system to be unpolarized places limits on how the electron density can evolve as strain is applied. In some systems, restricting the spin can lead to unphysical bondcleavage behavior.³¹ However, allowing for the possibility of polarization can more than double the computational resources required, and thus it is usually only done when necessary. To ensure that our results were not adversely affected, calculations for a 1.0 nm NW using RPBE/DZP were performed in which spin polarization was allowed. Figure 2 shows the stress-strain responses as predicted using RPBE/ DZP for a 1.0 nm NW, using both spin-restricted and unrestricted wave functions. The corresponding spin-restricted PBE/DZP result is also shown and is discussed later when the fracture mechanics associated with 1.0 nm NWs is discussed. The unrestricted calculations were intermittently performed in strain regions where failure was incipient in the restricted calculations. It is known that restricted wave functions are most likely to be inaccurate in these regions.³¹ As shown in Figure 2, it is clear that the stresses (and thus the energies of the structures that are used to



FIGURE 2. The stress-strain behavior of 1.0 nm NWs. Comparison of predictions from calculations in which the electron spin was restricted and unrestricted, and RPBE/DZP was used. Results from spin-restricted PBE/DZP calculations are also shown.

calculate them) are the same in corresponding restricted and unrestricted calculations. Therefore, the use of spin-restricted wave functions seems justified, so they were used in the remainder of the calculations.

Having learned how to perform reasonable DFT calculations based on tests on 1.0 nm wires, calculations on the larger-diameter wires were undertaken. Figure 3 compares the stress-strain response observed in 2.4 and 3.6 nm NWs when MM-BP and PBE/DZP approximations are employed. As shown in Figure 3a, PBE/DZP does not predict a stress drop at ${\sim}9\,\%$ strain, which is associated with the phase transition in the MM-BP calculations. The PBE/DZP results show that the pristine NWs can be deformed elastically to strains as high as $\sim 20\%$ before any significant stress relaxation occurs. Images of the atomic structure in the yzplane (dark blue atoms in Figure 3b) are shown for visualization of the phase transition (Figure 3c). Atomic configurations at various strain states are labeled using capital letters. Interestingly, the stress drop observed with the PBE/DZP at \sim 20% strain is also associated with a transition to the BCT phase rather than brittle fracture (Figure 3c, state F'). However, the NW does not undergo further loading as occurs with MM-BP. It is conceivable that the high-strain attained with PBE/DZP already accounts for the deformation that the transformed phase might have otherwise undergone. The qualitative behavior after 20% strain predicted by PBE/DZP and MM-BP is similar.

Figure 4a shows the results obtained using PBE/DZP for the three different wire diameters. A significant size effect is predicted. As the wire diameter increases, the modulus and strength decrease. Small increases in failure strains are also anticipated. The predictions of RPBE/DZP are qualitatively similar to those of PBE/DZP except that the peak stresses attained are lower (see Figures 2 and 4b). For comparison, the theoretical strength of bulk ZnO is also plotted in Figure 4b, which was calculated from the elastic modulus and the surface energies associated with the (0001) cleavage plane, namely, $\sigma_{\rm T} = (\gamma E/c)^{0.5}$. *E* is the bulk Young's modulus, γ is the surface energy of the (0001) planes, and *c* is the lattice constant along the loading direction. The peak

NANOLETTERS



FIGURE 3. (a) Stress—strain curves comparing the predictions of MM-BP and PBE/DZP for 2.4 and 3.6 nm NWs; (b) a schematic showing the atoms (in blue) that are plotted in (c) to illustrate the atomic rearrangement during the 2.4 nm wire phase transition; (c) snapshots showing the atomic structure at different strain steps.



FIGURE 4. (a) Size-dependent stress-strain response of NWs of different diameters, calculated using PBE/DZP. (b) Peak stress vs NW diameter, calculated using PBE/DZP and RPBE/DZP. For comparison, the calculated fracture stresses of bulk ZnO are also plotted.

stresses of the NWs decrease with increasing wire diameter, and they approach the bulk values monotonically (Figure 4b). It is worth noting that the postpeak stress mechanical behavior of the 1.0 nm wire was found to be qualitatively different from that predicted for larger wire diameters (Figure 4a). The larger wires did not exhibit a secondary loading regime beyond ~20% strain, which was observed for the 1.0 nm wires. Such high failure strains in the latter may be the result of their high surface-to-volume ratio, as there is just one chain of core atoms present in this case. It has been reported that nanotube morphologies can be more stable than nanowires for such small sizes,³⁶ signifying the effect of high surface-to-volume ratios.

Experimental verification of the size-dependence of the fracture stress will be challenging. These stresses are always influenced by the presence of pre-existing defects that arise during the growth process.¹ Even if wires could be fabricated defect-free, the simulations suggest that wires ≤ 5 nm in diameter would need to be tested to observe variations.

In any of the DFT calculations, there was no sign of the phase transition observed at a stress of ${\sim}20$ GPa and a strain

of ~10% at which MM-BP simulations predicted a transition. To further explore the possibility of this transition and the role of thermal fluctuations present at room temperature, we performed energy calculations on a 2.4 nm wire at a stress level of 20 GPa. Energy barriers were calculated using PBE/DZP and RPBE/DZP along simple transition paths. The possibility of a homogeneous transition was examined. Surface defects, which have been experimentally observed,¹ might serve as nucleation sites for the transition. Therefore, the possibility of a heterogeneous transition was also explored.

In both cases, the initial atomic configuration, $C_{\rm U}$, was stressed (~20 GPa) but untransformed. Two transformed configurations at 11 % strains were considered: (1) a completely transformed configuration representative of homogeneous transition, $C_{\rm T}^{\rm H}$ (Figure 5b (ii)); and (2) a partially transformed configuration representative of heterogeneous transition, $C_{\rm T}^{\rm D}$ (Figure 5b (iii)), involving ~68% of transformed atoms. Intermediate configurations were created as follows:



FIGURE 5. (a) Energy barriers required for phase transition of a 2.4 nm ZnO nanowire; (b) initial and final configurations used to calculate the energy barriers (dashed lines represent periodic boundary conditions along the axis of the wire); (c) a schematic illustrating heterogeneous nucleation in the vicinity of a surface defect. Surface defects have been shown to be present in experimentally tested ZnO nanowires.¹

1. Displacement vector u_i was obtained for each atom by taking the difference in atomic positions in the two configurations such that $u_i = (C_T)_i - (C_U)_i$.

2. N - 1 intermediate configurations were generated, assuming uniform scaling, such that the coordinates of each intermediate configuration were given by: $(C_l)_i = (C_U)_i + (u_i * j / N)$, where j = 1, ..., N - 1.

The energy barriers were estimated to be 42.3 and 34.3 eV for the case of homogeneous transformation with PBE and RPBE respectively and 19.3 eV for the heterogeneous case with RPBE. Interestingly, when the calculated energy barriers were normalized with respect to the number of atoms that underwent transition, the barriers per BCT atom were found to be below 0.1 eV (for RPBE). Figure 5a shows the energy barriers for the different cases after normalization. The most-probable thermal energy, $k_{\rm B}T$, where $k_{\rm B}$ is Boltzmann's constant and T = 300 K, is also plotted in Figure 5a. It is noteworthy that the energies of the final homogeneous and heterogeneous configurations, after normalization, are in good agreement. This asserts that the energy of final configuration scales with the number of transformed atoms, which also suggests that the barrier height should similarly scale with the number of transformed atoms. Accordingly, such normalization is a good estimator of the energy barrier in a heterogeneous transformation, the most likely scenario. The difference computed in the barrier heights for homogeneous (0.089 eV) versus heterogeneous (0.073 eV) transformation with RPBE may be attributed to the fact that these barriers were not calculated along the possible minimum energy paths.³⁷

The possible role played by surface defects remains an open and intriguing question. Surface defects (see Figure 5c) produce stress concentrations when wires are placed under strain. At the present time, quantum mechanical modeling of defects in nanowires remains a challenge because of the limited number of atoms used in the simulations and the use of periodic boundary conditions. Stress—strain response for a 2.4 nm nanowire of length 2c with a 3-ZnO pair vacancy defect reveals a reduction of ~2 GPa in fracture stress. Further investigation with longer wires is necessary to estimate the defect types and sizes which can lead to a

better agreement with experimentally observed fracture properties. $^{1} \ \ \,$

According to transition state theory, the probability of phase transition is proportional to $\exp(-Q(\sigma, T)/k_{\rm B}T)$, where $Q(\sigma, T)$ is the energy barrier, a function of stress, and temperature. In ref 38, the following functional form was proposed

$$Q(\sigma, T) = A \left(1 - \frac{T}{T_{\rm m}}\right) \left(1 - \frac{\sigma}{\sigma_{\rm ath}}\right)^{\alpha}$$
(2)

where $T_{\rm m}$ is the surface reordering temperature, $\sigma_{\rm ath}$ is the maximum stress required to overcome the barrier at 0 K, and *A* and α are fitting parameters dependent on the material system being studied. From the above equation, one can observe that the energy barrier reduces as the applied stress, σ , increases and approaches the athermal stress predicted by the DFT simulations here reported. Therefore, it can be argued that stress concentrations in the presence of defects might increase the probability of the WZ to BCT transition involving just a small number of atoms near the defect, which acts as a transition nucleation site. Random thermal motion might also initiate a local phase transition involving just a few atoms, once the wire is under sufficiently high stress.

The computational results reported here allow us to draw several conclusions: (i) NW peak stresses are diameter-dependent; (ii) the WZ-BCT phase transition is a precursor to fracture; (iii) the stress and strain state at which the WZ-BCT transition would occur can be estimated using transition state theory; (iv) the stress relaxation and accompanying phase transition at $\sim 10\%$ strain, observed in the MM-BP simulations even in the absence of defects, is an artifact of the Buckingham potential. This may be due to an inaccurate accounting for the energy costs associated with the angular and torsional distortion of bonds in the BP. These effects can be significant at large strains. A similar discrepancy between the findings of semiempirical force fields and QM-based reactive force

NANOLETTERS

fields has been reported in the context of fracture of silicon.^{39,40} In addition, a similar phenomenon of heterogeneous and local phase transition (formation of 5 and 7 atom rings) in the vicinity of a crack tip has been reported for this material.⁴⁰

As pointed out earlier, the BCT phase has not been observed experimentally. The DFT simulations suggest that a significant amount of energy will be stored in any NW-testing system before the transition will take place, which would be released upon transition. Because of current limitations in testing methodologies,¹ capturing this strain-state would be extremely challenging. Improvements in experimental tools, for example, displacement control at both ends of the sample and high-frequency image acquisition in situ TEM,⁴¹ are needed to increase the probability of capturing the phase transition phenomenon. In quantum mechanical simulations, modeling of defects requires longer NWs, as defects in short wires subjected to periodic boundary conditions can result in spuriously high defect densities. Defects in neighboring unit cells can interact, and these interactions can lead to unphysical behavior. The introduction of atomic displacements as a means of mimicking a thermal fluctuation in an otherwise-pristine wire would be no different than introducing other types of defects in terms of problems associated with unrealistic defect densities and interactions. Even if the model length is increased by just 4 times (i.e., to 8c) to avoid defect-defect interaction, it leads to more than 1500 atoms for 2.4 nm NW. From scaling studies, we extrapolate that modeling of all strain steps with 1500 atoms can take more than 2 months of computational time on 256 processors (which is equivalent to 0.37 million CPU hours for one case). Hence, current restrictions on the numbers of atoms that can be modeled using DFT, because of its computational cost, limit such studies. However, ongoing improvements in computational resources as well as the development of accurate multiscale methods should make such computations possible in the near future.

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