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Atomistic modeling of Phase transformation in ZnO nanorods

J. Y. He, S. Nagao, J. Y. Wu, Z. L. Zhang

NTNU Nanomechanical Lab, Department of Structural Engineering, Norwegian University of Science and Technology (NTNU), 7491, Trondheim, Norway.
jianying.he@ntnu.no, shijo.nagao@ntnu.no, jianyang.wu@ntnu.no, zhiliang.zhang@ntnu.no

Summary. Molecular dynamic simulations are performed to systematically investigate the structural□mechanical properties of ZnO nanorods (NRs) using the empirical Buckingham potential. The considered NRs have hexagonal cross-sections with lateral dimension ranging from 1-10nm and constant length 10.4nm. Different from its bulky counterpart, the results show that ZnO NRs undergo a size dependent four-stage deformation process: elastic stretching of initial Wurtzite structure, Wurtzite to body-centered tetragonal (BCT-4) phase transformation, stretching of the resulting BCT-4 structure and eventually brittle fracture. The critical stress for phase transformation decreases while the critical strain increases with increasing the NR size. The analyses indicate that the size dependency of phase transformation is dominated by the size effect on the Young's modulus.

Key words: ZnO Nanorods, molecular dynamic simulations, phase transformation, Young's modulus, fracture.

Introduction

Quasi-one-dimensional nanostructures made of semiconductors possess large potential applications in electromechanical devices because of the unique electrical and mechanical properties associated with their finite size [1]. In particular, ZnO nanostructures, such as nanorods (NRs), nanowires and nanobelts have received great attention due to their excellent performance in electronic, piezoelectric, ferroelectric and optical applications [2]. The mechanical, optical and electric as well as piezoelectric properties of ZnO have been experimentally investigated. However, experimental evaluation of mechanical properties at the nano-scale is full of challenges and uncertainties due to crystalline structure, sample manipulation, geometry condition, instrument calibration, and so on [3]. Instead, atomistic simulations provide an alternative way to predict the structural□mechanical properties of ZnO nanostructures [4]. While it is not observed in experimental study, a novel transformation from original Wurtzite to body-centered tetragonal (BCT-4) phase has been numerically discovered on ZnO NRs under tension along with <0001> axial orientation [4]. To clarify those

controversial results between experiments and simulations, molecular dynamics (MD) simulations using LAMMPS (Large-Scale Atomic/Molecular Massively Parallel Simulator) code are performed in this study to investigate the mechanical properties of ZnO NRs. In addition to the elastic property, the size-dependent phase transformation as well as the fracture behaviour of ZnO NRs under uniaxial tension is examined.

MD methods

Wurtzite ZnO NRs oriented in <0001> with hexagonal cross-sections were generated with the lattice constant a = 3.2501Å, c = 5.2071Å, and internal parameter u = 0.3817 [5]. The lateral dimension D of the NRs varied from 1.0, 1.8, 2.4, 3.0, and 5.0 to 10nm, while the length L was constant 10.4nm. Empirical Buckingham potential (equation (1)) with Binks parameters (Table 1) was adopted to describe the short-range atomic interactions [6]. As for the long-range Coulombic force, Ewald summation method was used.

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

Periodicity required for Ewald summation were imposed on three directions for accurate Coulombic force calculation, therefore a sufficiently large gap along lateral directions was given to avoid interactions between neighbouring NRs. After geometric construction, an annealing process with an integration time step of 1 fs was performed to relax the NRs under the ambient pressure (*NPT*) in <0001> direction to stabilize the ZnO NRs. The uniaxial tensile strain with strain rate of 0.001/ps was applied to the NRs by extending the length along the tension direction to 30% strain, under *NVT* conditions at 5K.

Table 1. Short-range interaction parameters for ZnO.

Species		A, eV	ρ, Å	C, eV Å
O^{2-}	O^{2-}	9547.96	0.21916	32.00
Zn^{2+}	O^{2-}	529.70	0.3581	0.00
Zn^{2+}	Zn^{2+}	0.00	0.00	0.00

Results and discussions

The stress–strain relationships for different sizes of ZnO NRs are compared in figure 1. The results suggest that the deformation process of ZnO NRs consists of four stages: elastic stretching represented by the initial linear region, a phase transformation indicated by the stress relaxation, stretching of the new phase structure, and eventual fracture by the secondary stress relaxation. The mechanical response of ZnO NRs is significantly size dependent during the entire deformation process. In an effort to clarify the size effect, the Young's modulus and the critical stress/strain for phase transformation are summarized as a function of the NR size in figure 2. The Young's modulus was obtained from the slope of the initial elastic region on stress–strain curves. Critical stress and strain for phase transformation were directly read the corresponding values at the starting points of the first stress relaxation.

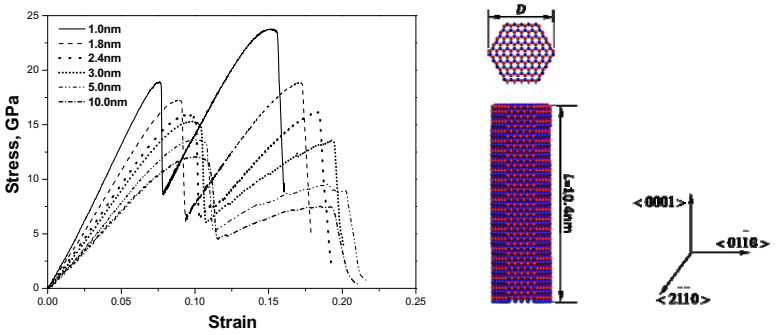
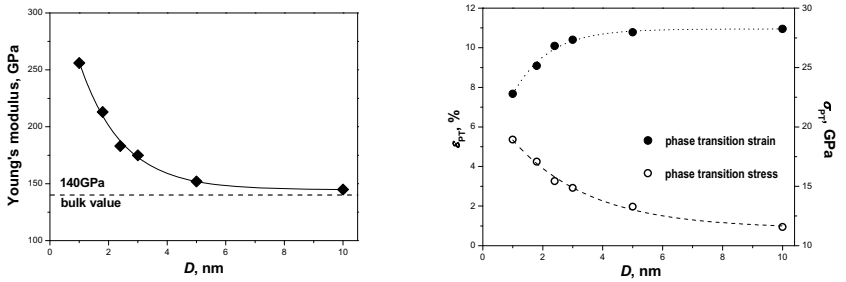


Figure 1. Stress□strain curves for sizes ranging from 1.0 to 10.0nm.



(a) (b)

Figure 2. Size-dependent mechanical properties of ZnO NRs: (a) Young's modulus and (b) critical strain and stress for phase transformation.

The Young's modulus of NRs within the sampling size is always higher than that of the bulk counterpart. With increasing the size from 1.0 to 10.0nm, the Young's modulus decreases from about 260GPa to 145GPa which approaches the bulk value. Within the size range from 1.0 to 10.0nm, the critical stress for phase transformation decreases about 40% while the strain increases 43%. Both critical stress and critical strain referred to different sizes of the NRs converge to a constant value when the size is sufficiently large.

During the uniaxial tension, the system temperature is kept constant 5K at which atomic vibrations are well suppressed so that the thermal effect on the ductility is minimized. All ZnO NRs display brittle fracture at a relatively high strain over 15%, as shown in figure 3. Comparing with the previous study, this cleavage fracture at high strain is unique for the hexagonal cross-sectional NRs, distinguished from the cylindrical NRs that exhibit super ductility [7], and also from the square cross-sectional NRs that display lower fracture strain around 6% [8]. The main reason is that the cylindrical and square cross-sectional NRs cannot keep close-packed hexagonal (HCP) lattice structure in wurtzite ZnO during equilibrium and are distorted to a twisted configuration and even an amorphous structure. Therefore the initial structure prior to deformation is not perfect Wurtzite.

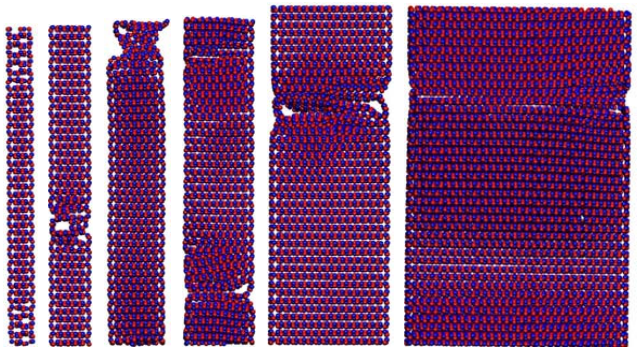


Figure 3. The fracture morphology of ZnO NWs with the size from 1.0 to 10.0nm.

Conclusions

Large-scale molecular dynamic simulation has been carried out to investigate the size-dependent mechanical properties of ZnO NRs. Under uniaxial tension, ZnO NRs possess a four-stage deformation process. In addition to the size-dependent Young's modulus reported by previous studies, the phase transformation is also influenced by the size of NRs. The critical stress for phase transformation drastically increases while the critical strain decreases as the NR size decreases. It suggests that larger NRs attempt to keep the original Wurtzite structure comparing with smaller ones.

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