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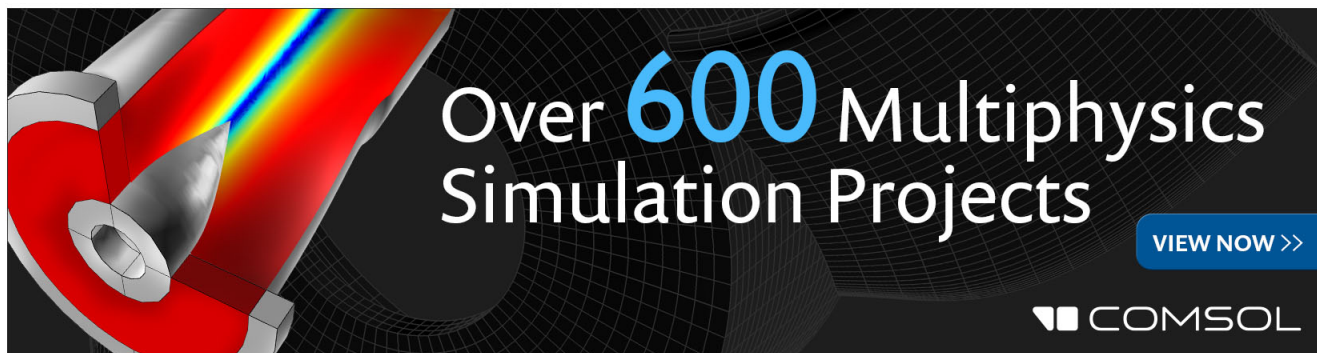
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Size dependency of the elastic modulus of ZnO nanowires: Surface stress effect

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Relation between the elastic modulus and the diameter (D) of ZnO nanowires was elucidated using a model with the calculated ZnO surface stresses as input. We predict for ZnO nanowires due to surface stress effect: (1) when $D > 20$ nm, the elastic modulus would be lower than the bulk modulus and decrease with the decreasing diameter, (2) when $20 \text{ nm} > D > 2$ nm, the nanowires with a longer length and a wurtzite crystal structure could be mechanically unstable, and (3) when $D < 2$ nm, the elastic modulus would be higher than that of the bulk value and increase with a decrease in nanowire diameter. © 2007 American Institute of Physics. [DOI: 10.1063/1.2821118]

One-dimensional (1D) ZnO nanomaterials have significant applications as active components in nanoelectromechanical systems.^{1,2} The elastic modulus of 1D ZnO nanomaterials determines how much elastic strain energy can be stored in their deformed states and further be utilized by nanodevices. However, there is no consensus about how the elastic modulus of 1D ZnO nanomaterials should depend on their geometry and size yet. Some experimental measurements strongly indicate that the elastic modulus of 1D ZnO nanomaterials (with sizes larger than 19 nm) is lower than that of bulk ZnO.^{3–7} In contrast, the results by Chen *et al.* show that the elastic modulus of ZnO nanowires with diameters ranging from 17 to 550 nm are higher than that of bulk ZnO and increase with the decrease of nanowire diameter.⁸ Atomistic modeling techniques have also been employed to study the elastic deformation in ZnO nanomaterials. Molecular dynamics simulations by Kulkarni *et al.* suggest that the elastic modulus of ZnO nanobelts with lateral dimensions from 1 to 4 nm are higher than the corresponding value of bulk ZnO and size-dependent.⁹ Zhang and Huang also found from their first-principles density functional theory (DFT) that the elastic modulus of ZnO nanoplates with thickness below 3 nm would be higher than those of bulk materials and increase as their size decreases.¹⁰

In this letter, we elucidate the size dependency of the elastic modulus of ZnO nanowires using the concept of surface stress. Surface stress is defined as the reversible work per unit area required to elastically stretch a surface, while surface energy is the reversible work per unit area required to create a surface.¹¹ In Ref. 12, the elastic modulus of a nanowire is proposed to be described in the following form:

$$E_{\text{nanowire}} = E_b + \frac{8}{5}g(1-\nu)\frac{L^2}{D^3}, \quad (1)$$

where, E_{nanowire} and E_b are the elastic modulus of the nanowire and bulk materials, respectively, L and D is the length and diameter of the nanowire, g is the surface stress, and ν is Poisson's ratio. Thus, a positive (tensile) surface stress would

lead to an increase in elastic modulus with the decreasing nanowire diameters, while a negative (compressive) surface stress would lead to a decrease in elastic modulus with the decreasing nanowire diameters. The above relation has been shown to be valid for Ag and Pd nanowires.¹²

Equilibrium ZnO has a wurtzite crystal structure. For its 1D nanomaterials grown along the [0001] direction, (10 $\bar{1}$ 0) and (11 $\bar{2}$ 0) surfaces are the lateral facets. In this work, we evaluated the surface stresses for the nonpolar (10 $\bar{1}$ 0) and (11 $\bar{2}$ 0) surfaces of ZnO using first-principles DFT method. The calculations were performed using the VASP code.^{13,14} We used the projector augmented wave method¹⁵ and the generalized gradient approximation of Perdew and Wang¹⁶ for exchange and correlation. We chose a kinetic energy cut-off of 600 eV to expand the electronic wave functions in the plane wave basis. For (10 $\bar{1}$ 0) surfaces, we used a supercell containing eight surface layers and eight layers of vacuum. There are two possible configurations for the (10 $\bar{1}$ 0) surface in a wurtzite crystal: (10 $\bar{1}$ 0)_A (whose outermost layer is separated from its sublayer by $(\sqrt{3}/6)a$, a is the lattice parameter in the base plane of ZnO lattice) and (10 $\bar{1}$ 0)_B (whose outermost layer is separated from its sublayer by $(\sqrt{3}/3)a$). For (11 $\bar{2}$ 0) surface, we used a supercell containing six surface layers and six layers of vacuum. For k -space integration, we used a $10 \times 6 \times 2$ k -point grid for (10 $\bar{1}$ 0) surface and a $6 \times 6 \times 2$ k -point grid for (11 $\bar{2}$ 0) surface.

The structure of ZnO surfaces was obtained through the relaxation of atomic positions using first-principles method. Significant relaxation in both (10 $\bar{1}$ 0) and (11 $\bar{2}$ 0) surfaces have been observed. Figures 1 and 2 show the top and side views of the relaxed (10 $\bar{1}$ 0) and (11 $\bar{2}$ 0) surfaces. In these figures, big circles represent Zn atoms while small circles stand for O atoms. For illustration, the atoms in the second layer of the surfaces are drawn in gray and the atoms in the third and fourth surface layers are plotted using dashed circles.

Surface energy (γ) and surface stress tensor (g) for the relaxed ZnO surfaces are calculated using the approach suggested in Ref. 17 and given in Table I. The surface energy of (10 $\bar{1}$ 0)_B surface is found to be much higher than the one of

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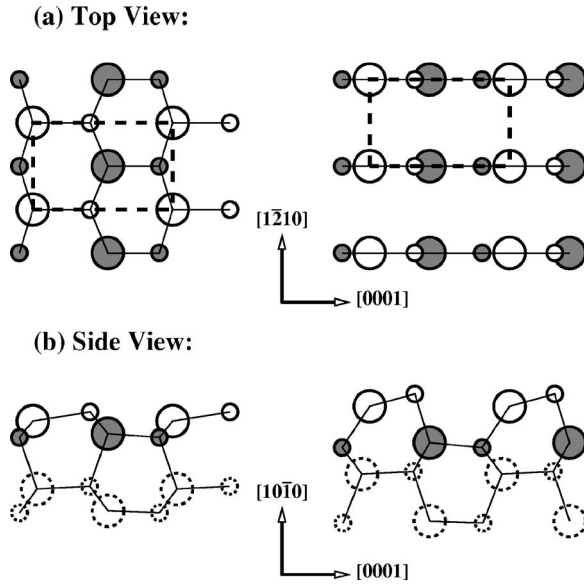


FIG. 1. (a) Top view and (b) side view of the relaxed $(10\bar{1}0)$ surfaces of ZnO. The left panels show the $(10\bar{1}0)_A$ surface and the right panels show the $(10\bar{1}0)_B$ surface.

$(10\bar{1}0)_A$ surface. This would lead $(10\bar{1}0)_A$ to be dominant in experimental $(10\bar{1}0)$ surface samples and hence we assume only $(10\bar{1}0)_A$ surfaces present in ZnO nanowires in this work. More importantly, the calculated surface stresses for the surfaces along the $[0001]$ direction are negative and have the same magnitude as the surface energies. Negative surface stresses indicate that the surfaces are in compressive states and thus energetically favor expansion. Since elastic deformation increases the surface areas, those surfaces with negative surface stresses would release energy during the deformation and lower the measured elastic modulus of 1D ZnO nanowires.

To examine the strain effect on surface energy and surface stress, we expanded ZnO $(10\bar{1}0)_A$ and $(11\bar{2}0)$ surfaces only along the $[0001]$ direction and relaxed the surface slabs at each given strain (ϵ). In Fig. 3, we plot the calculated surface energies and surface stresses as a function of the strains along the $[0001]$ direction. It is seen in Fig. 3 for the two surfaces that the surface energies decrease with the expansion strain up to about 2.5%, while the surface stresses

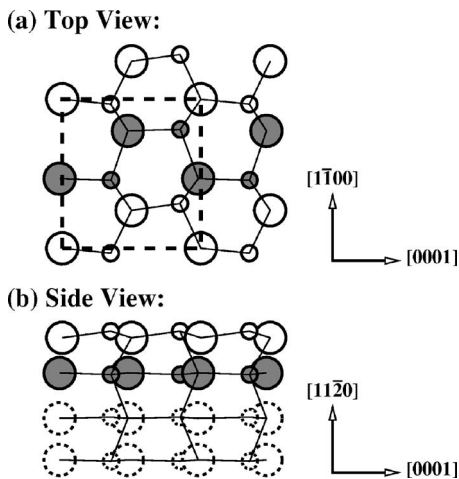


FIG. 2. (a) Top view and (b) side view of the relaxed $(11\bar{2}0)$ surface of ZnO.

TABLE I. Calculated surface energies γ (in J/m^2) and principal surface stresses g (in J/m^2) for nonpolar $(10\bar{1}0)$ and $(11\bar{2}0)$ surfaces of ZnO using first-principles method.

Surface		$(10\bar{1}0)_A$	$(10\bar{1}0)_B$	$(11\bar{2}0)$
γ		0.88	2.35	0.92
g	$[0001]$ axis	-1.13	-0.91	-0.81
	$[1\bar{2}10]$ axis	-1.23	0.03	...
	$[1\bar{1}00]$ axis	-0.34

(along the $[0001]$ direction) increase with the strain and change signs (from negative to positive) at the strain about 1.25%. Our results in Fig. 3 qualitatively point out that along the $[0001]$ direction, the nonpolar surfaces with a strain below 1.25% would facilitate elastic deformation and soften the elastic modulus of 1D ZnO nanomaterials. In contrast, the surfaces with a strain above 1.25% would hinder elastic deformation and harden the elastic modulus of 1D ZnO nanomaterials.

Furthermore, we derived the size dependency of the elastic modulus for ZnO nanowires enclosed only by either $(10\bar{1}0)_A$ or $(11\bar{2}0)$ surfaces.

(a) *Determination of the strain in surfaces.* The energy of ZnO nanowires per unit length is expressed as

$$U = U_0 + \frac{\pi D^2}{4} \Delta E_b(\epsilon) + \pi D \gamma(\epsilon), \quad (2)$$

where, U_0 is the energy of the equilibrium bulk ZnO with the same number of atoms as the nanowire, $\Delta E_b(\epsilon)$ is the energy density change with $[0001]$ strain for bulk ZnO, $\gamma(\epsilon)$ is the surface energy, and D is the diameter of the nanowire. Both $\Delta E_b(\epsilon)$ and $\gamma(\epsilon)$ were calculated using first-principles method and can be accurately fitted to quadratic functions: $\Delta E_b(\epsilon)$ has the minimum value at $\epsilon=0$ while $\gamma(\epsilon)$ [Fig. 3(a)] reach the minimum values at ϵ about 2.5%. Therefore, we could determine the strain (ϵ^*) in the ZnO nanowire surfaces through $(\partial U / \partial \epsilon)(\epsilon^*) = 0$.

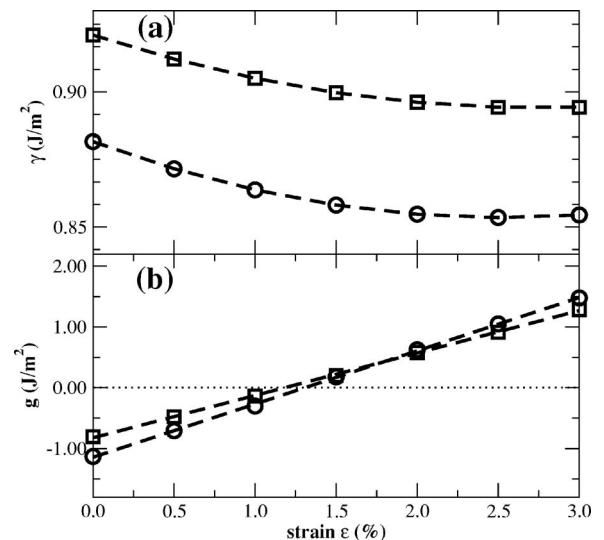


FIG. 3. Variation of (a) surface energies (γ) and (b) surface stresses (g) in $[0001]$ axis of ZnO surfaces with the strains along the $[0001]$ direction. Circles represent the data for $(10\bar{1}0)_A$ surface and squares represent the data for $(11\bar{2}0)$ surface. In panel (a), dashed lines are the fitting curves using a quadratic function. In panel (b), dashed lines are the linear fitting of the data.

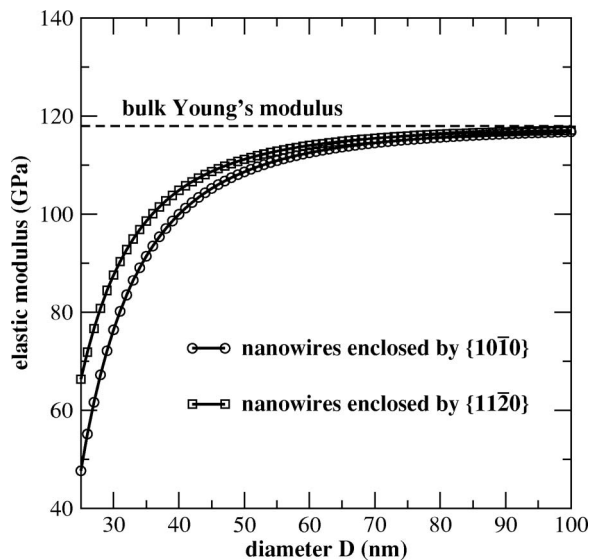


FIG. 4. Size dependency of the elastic modulus of ZnO nanowires enclosed by $(10\bar{1}0)_A$ surfaces (circles) or $(11\bar{2}0)$ surfaces (squares).

(b) *Determination of surface stress.* Figure 3(b) shows that the surface stresses of ZnO are linearly dependent on the strain ε^* in the surfaces.

(c) *Calculation of the elastic modulus of ZnO nanowires using Eq. (1).* In this work, we assume $L=1000$ nm, which is the typical suspended length of 1D ZnO nanomaterials in atomic force microscopy three-point bending tests.⁶ We also assume $E_b=118$ GPa and $\nu=0.32$ calculated using the experimental elastic constants.¹⁸

In Fig. 4, we plot the calculated elastic modulus of ZnO nanowires as a function of their diameters. It is predicted that due to surface stress effect, the elastic modulus of ZnO nanowires ($D>25$ nm) would be lower than the Young's modulus of bulk ZnO and decreases with the decreasing diameters. Our theoretical predictions are consistent with most of the early experimental measurements.^{3–7} Especially, our predictions agree excellently with the recent systematic measurements on the elastic properties of ZnO nanobelts.¹⁹ Figure 3(e) in that work shows that the elastic modulus of ZnO nanobelts is lower than the bulk value and will decrease with a decrease in their thickness (equivalent to nanowire diameter).

Our model was derived based on linear elasticity theory and could not accurately make quantitative predictions for small-diameter ($D<25$ nm) nanowires, in which nonlinear relaxation effect would be pronounced. Nevertheless, we can qualitatively discuss two issues using our model. (1) Our model gives negative elastic modulus for the ZnO nanowires with diameters below 20 nm but larger than 2 nm, implying those nanowires (with a wurtzite crystal structure and a length longer than 1000 nm) mechanically unstable. It seems to be consistent with the previous findings that ZnO nanomaterials would undergo a phase transformation from wurtzite to graphite crystal structures below some critical size.^{20,21} (2) For ZnO nanowires with a diameter below 2 nm, the predicted strains in their surfaces are larger than 1.25% and hence the surface stress will be positive. Our model predicts that the elastic modulus of those ZnO nanowires will be higher than the bulk value and increase with the decreasing nanowire diameters, agreeing well with the previous theoretical calculations.^{9,10}

As a further note, we anticipate that surface stress would play a similar role in determining the elastic modulus of some other wurtzite crystal 1D nanomaterials. For instance, it has also been experimentally found that 1D ZnS (Refs. 22 and 23) and GaN (Refs. 24–26) nanomaterials exhibit lower elastic modulus compared to their bulk values.

In conclusion, combining first-principles calculations and linear elasticity theory, we revealed that the surface enclosed large-diameter ZnO nanowires would release energy when stretched, and that is the reason for the measured low elastic modulus of 1D ZnO nanomaterials. Moreover, we pointed out that the surface stress would be positive and hence predicted enhanced elastic modulus for the small-diameter ZnO nanowires. In the context of surface stress, we resolved the “apparent” contradictions on the elastic property of ZnO nanomaterials between previous experimental measurements^{3–7} (which found low elastic modulus for large-size nanomaterials) and atomistic simulations^{9,10} (which predicted enhanced elastic modulus for small-size nanomaterials). Therefore, surface stress plays a very important role in determining the elastic modulus of 1D ZnO nanomaterials, suggesting that the elastic properties of nanomaterials could be engineered by altering the surface stress through rational control of the adsorptions, charges, structure, and impurities in the surfaces.

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