# Size Dependence of Young's Modulus in ZnO Nanowires

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We report a size dependence of Young's modulus in [0001] oriented ZnO nanowires (NWs) with diameters ranging from 17 to 550 nm for the first time. The measured modulus for NWs with diameters smaller than about 120 nm is increasing dramatically with the decreasing diameters, and is significantly higher than that of the larger ones whose modulus tends to that of bulk ZnO. A core-shell composite NW model in terms of the surface stiffening effect correlated with significant bond length contractions occurred near the $\{10\bar{1}0\}$ free surfaces (which extend several layers deep into the bulk and fade off slowly) is proposed to explore the origin of the size dependence, and present experimental result is well explained. Furthermore, it is possible to estimate the size-related elastic properties of GaN nanotubes and relative nanostructures by using this model.

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Nanowires have attracted considerable interest as nanoscale interconnects and active components of optical electronic devices and nanoelectromechanical systems (NEMS), etc. The size dependence of their mechanical properties is important for applying nanowires in NEMS, etc. and attracted much attention.

Experimentally, the bending modulus of carbon nanotubes (CNTs) [1] and Young's modulus of Ag and Pb NWs [2] are found to increase dramatically with decreasing diameters. However, investigations on Cr and Si nanocantilevers show an opposite tendency [3,4]: their moduli decrease sharply with decreasing diameters. The investigations on *SiC* nanorods [5] and Au NWs [6] suggest that their Young's moduli do not depend on diameters essentially.

Theoretical studies are through direct atomistic simulation [7–10] or corrections to continuum theory [2,11,12] to extract the overall mechanical response of a nanostructure. The elastic response of nanostructures has been explained by nonlinear effects [8], surface stresses [2,8,9], and surface elasticity [11,12]. By atomistic simulation, Miller and Shenoy [12] determined a proportionality constant relating with the surface elasticity for Si and Al nanobeams and explained their size dependent Young's modulus, but gave no account about what is the physical origin responsible for the softening or stiffening [10].

In spite of these experimental and theoretical results, corresponding investigations on oxide are rather scarce. Recently, the nanomechanical behaviors of one-dimensional ZnO nanomaterials have become the focus of several experimental [13–15] and theoretical [16] researches. Bai *et al.* [13] obtained an average Young's modulus equal to 52 GPa in [0001] oriented ZnO nanobelts. Yum *et al.* [14] investigated the dynamic behavior of cantilevered ZnO nanobelts with the same [0001] orientation; by the provided resonant frequencies the Young's modulus can be calculated as 38–100 GPa. Most recently by using atomic force microscopy (AFM) Song *et al.* [15] investigated elastic modulus of vertically aligned [0001] ZnO NWs with an average diameter of 45 nm and arrived at an average value of 29 ± 8 GPa. No obvious size effects had been discovered in these reports and the obtained values are far smaller than that of bulk ZnO, which is at the order of 140 GPa in [0001] direction. Recent molecular dynamics (MD) simulations performed by Kulkarni *et al.* [16] on tensile response of ZnO nanobelts with lateral dimensions smaller than 4 nm show an increasing modulus (which is higher than corresponding bulk value) with decreasing diameters.

In this Letter the Young's modulus of ZnO NWs with diameters ranging from 17 to 550 nm has been investigated. The electric-field-induced resonance method [1] is served in our experimental measurement. Consequently a size dependence of Young's modulus in ZnO NWs is experimentally revealed, and a theoretical model is proposed to explain the physical origin of the size effect.

ZnO NWs with a large range in diameters and a uniform [0001] growth orientation are fabricated by a controllable thermal evaporation procedure [17]. The as synthesized NWs are high quality single crystals having a wurtzite (WZ) structure with lattice constants $a = 3.249$ Å and $c = 5.206$ Å [17]. The typical lengths of the NWs are in the range of 7–15 $\mu$m. To facilitate the manipulation of individual NWs a cylindrical substrate is used so that free-standing NWs nearly vertically grown from the substrate are obtained [17]. The cylindrical substrate with NWs is mounted directly onto the specimen stage inside a scanning electron microscope (SEM). A homemade nanomanipulator with a sharp tungsten tip [18] is used to approach an individual NW. A frequency tunable ac voltage (having a frequency resolution 1 $\mu$Hz) with or without dc bias is applied across the NW and the countering tip. The resonance is directly monitored on the screen of the SEM.

It is critical to determine the fundamental natural frequency $\omega_0$ of a cantilevered NW, namely, critical to distinguish between forced resonance and parametric resonance. Forced resonance occurs at driving frequency $\omega = \omega_0$, while parametric instability occurs at $\omega = 2\omega_0/n$ ($n$ integer larger than 1) [19]. The extremely small dimensions of nanostructures make it very sensitive to parametric excitation [20–22]. For a NW with random orientation relative to the applied electric field, either parametric resonance or forced resonance may be excited. Failing to properly distinguish between these two types of resonances will lead to incorrectly determined natural frequency, which may be $2/n$ ($n = 1, 2, 3, 4$ can be observed readily in our experiments) times the true natural frequency, and results in very large deviation of the modulus, since the Young's modulus is proportional to the square of the frequency.

Yu *et al.* [21] has observed multifrequency resonance of a NW excited by an alternating electric field and ascribed it to parametric vibration; however, those parameters were not endowed with explicit physical meanings; Liu and Tripathi [22] modeled the parametric resonance of a carbon nanotube based on its polarization under electric field. They treated the CNT as vertically located between two parallel electrode plates. This is not so realistic for a dynamically measured NW. We report here a useful method to distinguish between parametric resonance and forced resonance; thus the uncertainty of the natural frequency is avoided.

We fabricated very sharp tungsten probes with typical tip radii ranging between 20–100 nm, which is necessary for the subsequent distinguishing between the two types of resonance. Our experiments reveal that the occurrence of parametric resonance is determined by the relative orientation of the NW to the countering tip, and actually by the direction of the force applied to the NW. As shown in Fig. 1, if the NW is aligned (arranged in a line) with the tip, resulting in an axially applied force, parametric excitation dominates, while if the force is applied transverse to the NW length, forced excitation dominates. This is consistent with the parametric resonance of a macroscopic beam under periodic axial load, which is a typical subject of parametric instability [19].

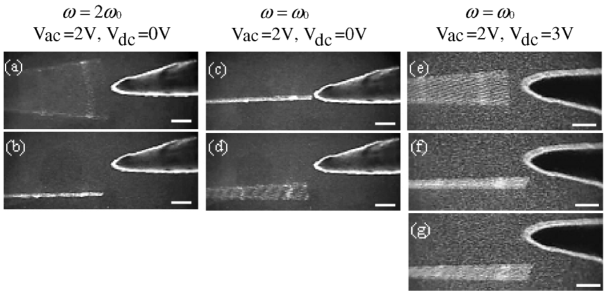


FIG. 1. Selected frames of a video recording the frequency responses of a NW subjected to (a), (c), (e) axial excitation, and (b), (d), (g) transverse excitation, showing: parametric resonance of (a) first order at $\omega = 2\omega_0$ and (e) second order at $\omega = \omega_0$ under axial excitation (the second order require a much higher dc voltage of 3 V); forced resonance (d) and (g) occurred at $\omega = \omega_0$ under transverse excitation; (f) transition from parametric to forced vibration. Scale bars represent 1 $\mu$m.

The measured values of the Young's modulus $E$ of ZnO NWs are shown as a function of the diameter in Fig. 2. For an anisotropic beam the value obtained through the resonance-based method is the effective axial Young's modulus [23]. For the wurtzite ZnO with hexagonal symmetry there are five independent elastic constants $c_{ij}$ ($i, j$ run from 1 to 6). The Young's modulus in [0001] direction can be expressed as:

$$E_3 = c_{33} - 2c_{13}^2/(c_{11} + c_{12}). \qquad (1)$$

Substituting the elastic constants given in Ref. [24] to Eq. (1) gives $E_3 = 140$ GPa for bulk ZnO.

As shown in Fig. 2, for NWs with larger diameters $D$ ($>$ about 120 nm) the measured Young's modulus is slightly dependent of the diameter and tends to the value of bulk ZnO, while the $D$ is decreasing from 120 nm down to 17 nm the measured values are dramatically increasing. No obvious tendency of Young's modulus to change with the length is observed.

Since our experimental NWs are high quality single crystals with few defects, it is expected that such a phenomenon of size dependence may originate from surface modification of NWs, as the surface effect becomes significant due to the large surface-to-volume ratio. One thing should be noted is that flexural deformation (vibration) is the case where the surfaces carry the largest stresses and strains due to their larger distance from the neutral axis. For this reason the surface elasticity may have a more pronounced contribution to the effective stiffness than an axial monotonic deformation does.

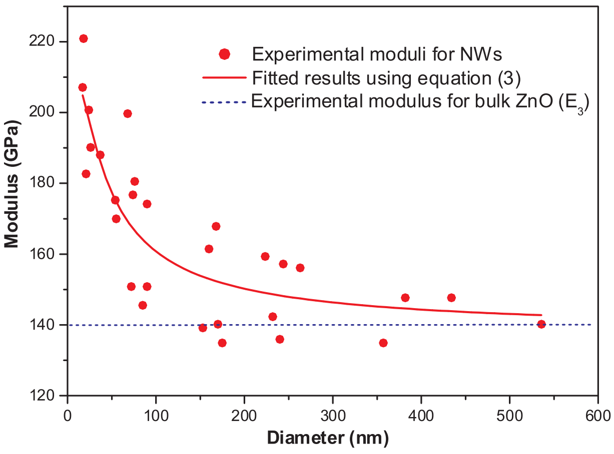


FIG. 2 (color online). Diameter dependence of effective Young's modulus in [0001] oriented ZnO nanowires for bending: (red dot) experimental results, (solid line) fitted results by the core-shell composite NW model, (blue dashed line) modulus for bulk ZnO ($E_3$) calculated using the experimental data from Ref. [24].

The ZnO $(10\bar{1}0)$ surfaces which are the lateral facets of our experimental NWs can be considered as consisting of rows of Zn-O dimers parallel to the [0001] direction, which are then bonded to dimers in its subsequent layer. Extensive theoretical and experimental results [25–28] on surface structure of ZnO show that the nonpolar $(10\bar{1}0)$ free surfaces undergo significant relaxation characterized by bond length contractions which amount up to 8% and 5%, respectively, for the in-plane and backbonds of the Zn-O dimers [26,27], and significant bond contractions extend at least five or six layers below the film surface [27].

This relaxation may have a prominent effect on the surface elastic properties, since the elastic constants of crystals are indeed very sensitive to the interatomic distance $d$ [29,30]. In bulk materials the elastic constants follow approximately a variation of $d^{-4}$ [29,30]. At the surface the effect of the reduced coordination number of the atoms should also be involved. Recent Bond-OLS (bond-order-length-strength) correlation analysis performed by Sun *et al.* [31] shows that the imperfect coordination number causes the remaining bonds of the lower coordinated surface atoms to relax and raises the binding energy; as a result, the effect of bond contractions at the surface will be more significant than that in a bulk one.

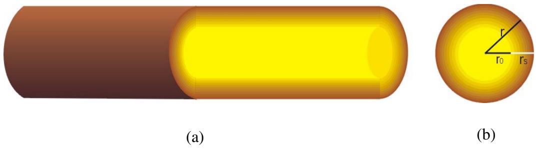
A NW with modified surface layers can be treated as a composite wire shown in Fig. 3 with a core-shell structure composed of a cylinder core having modulus of bulk material $E_0$ and a surface shell coaxial with the core but having a surface modulus $E_s$ which is correlated to the surface bond length contractions. It is noticed that the surface effect extending deep into the bulk is a gradual process and fades off slowly; however, to simplify the problem and without influencing the analysis of the problem, we treat the relaxed surface layers approximately as a uniform shell possessing an average bond contraction $\Delta\bar{d}$ through the overall thickness. Consequently the size-related elastic properties can be analyzed in terms of the approximate core-shell composite NW model.

Flexural rigidity is the governing parameter for transverse deformation. We define $EI$ as the effective flexural rigidity of the composite NW, with $E$ the effective Young's modulus in the axial direction. Neglecting shear deformation, we obtain:

$$EI = E_0 I_0 + E_s I_s, \tag{2}$$

where $I_0$ and $I_s$ are the moment of inertia of cross section of the core and the shell, respectively. Substituting $I_0$ and $I_s$ to (2) expanding and rearranging we obtain:

$$E = E_0\left[1 + 8\left(\frac{E_s}{E_0} - 1\right)\left(\frac{r_s}{D} - 3\frac{r_s^2}{D^2} + 4\frac{r_s^3}{D^3} - 2\frac{r_s^4}{D^4}\right)\right], \tag{3}$$



(a)

(b)

FIG. 3 (color online). (a) Schematic illustration of the core-shell composite NW model; (b) the cross section.

where $r_s$ is the depth of the shell and $D$ the NW diameter.

Equation (3) is used to fit the experimental results; the fitting curve is also shown in Fig. 2. It can be seen that the tendency of the Young's modulus versus the NW diameter described by Eq. (3) derived from the core-shell composite NW model fits reasonably well with the experimental results. The optimized curve fitting yields the values for three parameters, namely, $E_0 = 139$ GPa, $E_s/E_0 = 1.50$, and $r_s = 4.4$ nm.

The obtained $E_0$ value is quite close to the bulk value $E_3 = 140$ GPa calculated from the experimentally determined elastic constants from Ref. [24].

The value $E_s/E_0$ is a critical parameter determining the tendency of the size dependence of the Young's modulus. According to the bond-OLS analysis of Sun *et al.* [31,32] the correlation between surface modulus and the bond contraction can be described as:

$$(E_i - E_0)/E_0 = b_i^{-m} - 3b_i + 2, \tag{4}$$

where $E_i$ and $E_0$ are the Young's moduli of the $i$th atomic layer and bulk materials, respectively; $b_i$ is defined as $d_i/d_0$, with $d_i$ and $d_0$ the bond length in the $i$th layer and the bulk value, $m$ is a parameter used to describe the change of the binding energy, for compound and alloys $m \approx 4$ [31,32].

As mentioned above we assume an average bond length contraction $\Delta\bar{d}$ for the shell. Substituting $m = 4$, $d_0 = 1.99$ Å [26] (which is consistence with the lattice constants of the experimental NWs), and $E_s/E_0 = 1.50$ into Eq. (4) we obtain $\Delta\bar{d} = 0.13$ Å. This value is smaller than the largest bond contraction 0.16 Å which occurs at the outmost surface layer [26], and seems reasonable at least on a qualitative level. However, Eq. (4) is still an approximation [31,32]; therefore, the obtained $\Delta\bar{d} = 0.13$ Å is a rough estimation.

The value $r_s = 4.4$ nm obtained through curve fitting implies that a NW with diameter of about 8.8 nm will be fully relaxed and have an effective modulus equal to $E_s$, and it is expected that our model is applicable for diameters larger than 8.8 nm. Recently Kulkarni *et al.* [16] performed MD simulations on tensile response of [0001] oriented nanobelts with lateral dimension smaller than 4 nm and enclosed by $\{11\bar{2}0\}$ and $\{10\bar{1}0\}$ lateral surfaces. At so small dimensions our model may not work since the corresponding relaxation behavior is still much unclear and remains an open question.

Extension of the present analysis to elastic properties of other NW structures with a modified surface structure is possible. For example, the GaN with also a WZ structure has a surface relaxation similar to that of ZnO due to the strong ionicity arising from the existence of the first row element N just as O for ZnO [33–35], with an in-plane bond length contraction in the nonpolar $\{10\bar{1}0\}$ surfaces up to 7.4% [35], which allows us to predict an increasing modulus of GaN NWs with decreasing diameters. This is confirmed by the most recent energetic calculations performed by Xu *et al.* [36] on single crystal GaN nanotubes having a WZ structure and with nonpolar $\{10\bar{1}0\}$ lateral facets. Their calculations reveal a significantly increased modulus with increased surface-to-volume ratio.

In summary, a size dependence of Young's modulus in [0001] oriented ZnO NWs is experimentally revealed. The Young's modulus of ZnO NWs with diameters smaller than about 120 nm increases dramatically with decreasing diameters, and is significantly higher than that of the larger ones whose modulus tends to that of bulk ZnO. An approximate core-shell composite NW model in terms of the surface stiffening effect arising from the gradually shortened bond lengths from the bulk core to the outmost surface is proposed, through which the size dependence of Young's modulus is well explained. It is possible to extend the core-shell model to estimate the size dependence of Young's modulus in relative nanostructures such as single crystal GaN nanotubes.

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