Size-induced elastic stiffening of ZnO nanostructures: Skin-depth energy pinning

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It has long been puzzling regarding the trends and physical origins of the size-effect on the elasticity of ZnO nanostructures. An extension of the atomic “coordination-radius” correlation premise of Pauling and Goldschmidt to energy domain has enabled us to clarify that the elastic modulus is intrinsically proportional to the sum of bond energy per unit volume and that the size-induced elastic stiffening arises from (i) the broken-bond-induced local strain and skin-depth energy pinning and (ii) the tunable fraction of bonds between the undercoordinated atoms, and therefore, the elastic modulus of ZnO nanostructures should increase with the inverse of feature size. © 2009 American Institute of Physics. [DOI: 10.1063/1.3109786]

The intriguing elastic behavior of ZnO nanostructures has attracted tremendous interest in recent years because of its fundamental importance and its practical applications in fields such as nanomechanoelectronic devices.1–4 Young’s modulus $Y$, which is related to the performance of a material such as the elasticity, extensibility, acoustic transmission velocity, Debye temperature, specific heat, and thermal conductivity of the specimen, is a constant valued at 140 GPa at a room temperature for a bulk ZnO.5 However, with miniaturization of its size down to nanometer scale, the Young’s modulus decreases from $Y$ to $Y_{\text{nano}}$, which is related to the performance of a material such as the elasticity, extensibility, acoustic transmission velocity, Debye temperature, specific heat, and thermal conductivity of the specimen, is a constant valued at 140 GPa at a room temperature for a bulk ZnO.5 However, with miniaturization of its size down to nanometer scale, the Young’s modulus of ZnO becomes tunable with the shape and feature size. Different trends of size dependence have been reported.4–23 One kind of observation is that the Young’s modulus of ZnO nanowires, nanotubes, nanobelts, nanofibers, nanorods, nanofilms, and nanocrystals increases with the inverse of features size $6–12$. However, some results suggest that no obvious size effects was observed or size induces elasticity depression.15–17 The size-induced elastic change in nanomaterials was attributed to the effects of the high surface-to-volume ratio,5 surface stresses,6,8,9,18 bulk nonlinear elasticity,9 surface stiffness,4,11,18–20 surface tension,18 surface reconstruction,21 surface strain,22,23 etc. Therefore, clarification of the size-induced trend of change and consistent understanding of the mechanism behind is highly desirable. The objective of this work is to show that the elastic modulus is intrinsically proportional to the sum of bond energy per unit volume and that the size dependence of the Young’s modulus arises from (i) the broken-bond-induced local strain and energy trapping and (ii) the tunable fraction of lower-coordinated atoms in the surface of skin depth yet bonds in the core interior remain as they are in the bulk, making no contribution to the size effect.

First, we show that the elastic modulus is intrinsically proportional to the energy density. Given the Lenard-Jones potential $u(r)$, for example, and taking the atoms as spheres with radius $(r)$ and the equilibrium bond length $(d)$, the bulk modulus can be derived as

$$B = -V\frac{\partial P}{\partial V}\bigg|_{vd} = -V\frac{\partial P}{\partial V}dr = -V\frac{\partial u(r)}{\partial r}\frac{dr}{dV}$$

where $P = -\partial u(r)/\partial V$ is the pressure. At equilibrium, $P=0$ and $\sigma=0.8989d$. The relation between elastic modulus and bulk modulus is $Y \approx 3B$ if the Poisson ratio is negligibly small. Therefore, the elastic modulus is intrinsically proportional to the energy density. One can change the local modulus by varying the bond energy and/or bond length. This relation applies to any kind of interatomic potential as the modulus is related only to the bond length and energy at equilibrium.

Second, the surface-to-volume ratio $\gamma_i$ determines the trend of size dependence. Taking a sphere with radius $R$ as a sample, the surface-to-volume ratio can be derived for the first atomic shell of $d_i$ thick,

$$\gamma_i = f_{V_i}^V dV = f_{V_i}^V dV = \frac{4\pi R^3}{3} - \int_{R}^{d_i} dr = \frac{3 c_i}{K},$$

where $K$ is the number of atoms lined along the radius of the nanosphere or across the thickness of a thin film or the wall thickness of a nanotube. $c_i$ is the bond contraction coefficient that varies only with the effective coordination number $z_i$ of the atom of concern. Generally, $\gamma_i = \pi c_i/K$. $r=1, 2$, and $3$ correspond to a thin plate, a cylindrical rod, and a spherical dot, respectively. If all bonds in the nanocrystal contribute to the elastic enhancement, the integral over the range from $R=0$ to $R$, Eq. (2) becomes unity. Therefore, the measured $1/K$ dependence of elastic modulus indicates clearly the
TABLE I. The table lists the A, B, and the calculated m values for the ZnO nanostructures of different shapes. The inconsistency in the m values originates from the calculation methods depending on the interatomic potentials.

<table>
<thead>
<tr>
<th>nanostructures</th>
<th>A</th>
<th>B</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanowires (τ=2)</td>
<td>140+21.51</td>
<td>380.85</td>
<td>2.8</td>
</tr>
<tr>
<td>Nanorods (τ=2)</td>
<td>140+34.74</td>
<td>504.31</td>
<td>4.0</td>
</tr>
<tr>
<td>Nanotubes (τ=2)</td>
<td>140+25.26</td>
<td>210.42</td>
<td>0.6</td>
</tr>
<tr>
<td>Nanofilms (τ=1)</td>
<td>140+29.89</td>
<td>240.8</td>
<td>1.0</td>
</tr>
<tr>
<td>Nanobelts</td>
<td>140+22.58</td>
<td>154.29</td>
<td>1.9</td>
</tr>
<tr>
<td>Nanorods (τ=2)</td>
<td>140+25.18</td>
<td>145.76</td>
<td>1.7</td>
</tr>
<tr>
<td>Nanotubes (τ=2)</td>
<td>140+24.15</td>
<td>168.05</td>
<td>2.2</td>
</tr>
<tr>
<td>Nanofilms (τ=1)</td>
<td>140+19.23</td>
<td>294.43</td>
<td>4.3</td>
</tr>
<tr>
<td>Nanobelts</td>
<td>140+11.36</td>
<td>187.16</td>
<td>2.3</td>
</tr>
<tr>
<td>Nanorods (τ=2)</td>
<td>140+19.23</td>
<td>294.43</td>
<td>4.3</td>
</tr>
<tr>
<td>Nanotubes (τ=2)</td>
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<td>2.3</td>
</tr>
</tbody>
</table>

Reference 21.
Reference 10.
Reference 7.
References 11 and 20.
Reference 8.

bonds in the surface shell of limited thickness dominate the size-induced change.

Finally, the size dependence of elastic modulus originates from the broken-bond-induced local strain and skin depth energy pinning according to the bond-order-length-strength (BOLS) correlation, which is an extension of the atomic “coordination-radius” correlation premise of Pauling and Goldschmidt. If one bond breaks, the remainder between the undercoordinated atoms becomes shorter and stronger. The bond length contracts from the bulk value of \(d\) to \(d_i = c_id\) and the bond energy will increase from the bulk value of \(E_B\) to \(E_i = c_i^{-m}E_B\). The index \(m\) is the bond nature indicator but it is not freely adjustable for a specific material. The subscripts \(i\) and \(b\) denote an atom in the \(i\)th atomic layer and in the bulk, respectively. The \(i\) is counted from the outermost atomic layer up to three to the center of the solid, as no bond order loss occurs for \(i > 3\). The \(z_i\) being the effective coordination number of the specific \(i\)th atom varies with the size or the curvature of a nanostructure: \(z_1 = 4(1 - 0.75/K)\), \(z_2 = z_1 + 2\), and \(z_3 = 12\).

For a nanosolid of volume \(V\) with a characteristic size \(K\), the modulus can be expressed as

\[
Y(K) = VY_0 + \sum V_i(y_i - y_0),
\]

where \(y_0\) and \(y_i\) correspond to the local Young’s modulus inside the bulk and in the \(i\)th atomic site, respectively. \(V_i\) is the volume of the \(i\)th atomic shell. Combining Eqs. (1)–(3), we have a general form

\[
\frac{\Delta Y(K)}{Y(\infty)} = \sum_{i \leq 3} y_i(c_i^{-m+3} - 1) = \frac{\tau}{K} \sum_{i \leq 3} c_i^{-m+3} - 1.
\]

The weighing factor \(y_i(K, \tau, z_i)\) represents the geometrical contribution from size, dimensionality, and effective coordination, which determines the trend of change. The \(c_i\) originates the size dependency. If \(c_i = 1\), the elasticity will not change.

In comparison with the measured size that can be expressed as \(Y(K) = A + BK^{-1}\), we have

\[
\Delta Y(K) = \frac{Y(K)}{Y(\infty)} = \frac{Y(K)}{A + BK^{-1}}.
\]

\[
\Delta Y(K) = \left(1 + \frac{Y(K)}{A + BK^{-1}}\right)^{-1} = \frac{A + BK^{-1}}{A + BK^{-1}} = \frac{A + BK^{-1}}{A + BK^{-1}}.
\]

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\Delta Y(K) = \left(1 + \frac{Y(K)}{A + BK^{-1}}\right)^{-1} = \frac{A + BK^{-1}}{A + BK^{-1}} = \frac{A + BK^{-1}}{A + BK^{-1}}.
\]

\[
\Delta Y(K) = \left(1 + \frac{Y(K)}{A + BK^{-1}}\right)^{-1} = \frac{A + BK^{-1}}{A + BK^{-1}} = \frac{A + BK^{-1}}{A + BK^{-1}}.
\]

where \(A = Y(\infty)\) and \(B = A^{-1} = A\) is the slope of the linear dependence of the elastic modulus on \(K^{-1}\).

In numerical processing, we plot the measured \(Y - K^{-1}\) to find \(A\) and \(B\) with the known value \(A = Y(\infty) = 140\) GPa and bond length \(d_0 = 0.199\) nm to calibrate the reported data (Table I). An offset of the measured data is necessary because the relative change \(\Delta Y(\infty)/Y(\infty) = 0\). By using the relation of \(BA^{-1} = \tau\Delta\), we can calculate the values of \(\Delta\) and hence determine the \(m\) (Fig. 1).

In the current work, we simulated the size dependence of \(Y(K)\) for ZnO nanowires with cylindrical and hexagonal cross sections, nanotubes, nanobelts, and nanofilms for comparison. Only the outermost three atomic layers are considered for ZnO nanowires, nanorods, and nanofilms but for...
ZnO nanotubes, we should consider the contribution of both the outer and the inner shells. Comparison between theoretical and simulation results is given in Fig. 2. Exceedingly good agreement has been attained for ZnO nanowires, nanotubes, nanofilms, and nanobelts.

Agreement between predictions and observations confirmed that (i) the elastic modulus is intrinsically proportional to the binding energy density, (ii) the size induced trend is determined by the surface-to-volume ratio, (iii) only the outermost three atomic layers contribute to the elastic enhancement yet bonds in the core interior remain as they are in the bulk, and (iv) the broken-bond-induced local strain, the skin depth energy pinning, and the tunable fraction of lower-coordinated atoms in the surface of skin depth dominate the elastic modulus enhancement. The observed multiple trends of change may arise from experimental techniques and operation conditions in measurement. The energy potential well depression near the edge in calculation is highly recommended. For a given material, only one trend of the size-induced stiffening is correct.

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