Modeling Nanomechanical Behavior of ZnO Nanowires as a Function of Nano-Diameter

L. Achou, A. Doghmane

Abstract—Elastic performances, as an essential property of nanowires (NWs), play a significant role in the design and fabrication of modern nanodevices. In this paper, our interest is focused on ZnO NWs to investigate wire diameter ($D_{\text{wire}} \leq 400$ nm) effects on elastic properties. The plotted data reveal that a strong size dependence of the elastic constants exists when the wire diameter is smaller than ~100 nm. For larger diameters ($D_{\text{wire}} > 100$ nm), these ones approach their corresponding bulk values. To enrich this study, we make use of the scanning acoustic microscopy simulation technique. The calculation methodology consists of several steps: determination of longitudinal and transverse wave velocities, calculation of reflection coefficients, calculation of acoustic signatures and Rayleigh velocity determination. Quantitatively, it was found that changes in ZnO diameters over the ranges $1$ nm $\leq D_{\text{wire}} \leq 100$ nm lead to similar exponential variations, for all elastic parameters, of the from: $A = a + b \exp(-D_{\text{wire}}/c)$ where $a$, $b$, and $c$ are characteristic constants of a given parameter. The developed relation can be used to predict elastic properties of such NW by just knowing its diameter and vice versa.

Keywords—Elastic properties, nanowires, semiconductors, ZnO.

I. INTRODUCTION

ZnO NWs with unique properties intrinsically associated with low dimensionality, size confinement, and large surface area to volume ratio are very promising for applications in electronic, optoelectronic, and sensor devices. The key material property reflecting the NW’s elasticity. Secondly, it is one of the intrinsic parameters of each material: in macroscopic systems, it is constant ($140$ GPa) [4], but at the nanometer scale, it depends on the nano-diameter. Finally, the determination of the Young’s modulus leads to the determination of other elastic parameters such as the shear modulus, bulk modulus, and surface acoustic wave (SAW) velocities.

Depending on the size of objects and the type of mechanical property studied, various theoretical methods and experimental techniques (under different loading modes) have been developed to investigate the nanomechanical behavior [5]. In spite of this great deal of interest, there is neither a theoretical equation nor a single model to predict the relation between size and elastic parameters in ZnO NWs.

In this context, the nano-diameter dependence of the elastic properties of ZnO NWs oriented along the [0001] direction is studied. We first consider the commonly used mechanical characterization methods for measurement/calculation of the Young’s modulus of NWs (with $D_{\text{wire}} \leq 400$ nm). Then, we investigate the NWs by scanning acoustic microscopy (SAM) technique [6], [7] based on the emission and reflection of SAWs to determine the effects of $D_{\text{wire}}$ on acoustic velocities. We also calculate reflection coefficients and acoustic signatures for ZnO NWs. Finally, an expression relating diameter to such acoustic parameters is suggested.

II. COMPUTATIONAL APPROACH

The procedure consists of the following steps:
(a) Data choice: Survey, select and exploit the Young’s modulus data measured/calculated by the frequently used experimental/theoretical methods reported in the literature [3], [5], [8]-[11];
(b) Quantification of wire diameter effects on Young’s modulus: Plot the data as a function of $D_{\text{wire}}$ (with $1$ nm $\leq D_{\text{wire}} \leq 400$ nm) and then determine an analytical relation $E = f(D_{\text{wire}})$ in the initial region where the size effects are very important;
(c) Determination of other elastic parameters: Evaluate the diameter effects on the following elastic parameters: shear modulus, $G$, bulk modulus, $B$, Poisson’s ratio, $\nu$, longitudinal wave velocities, $V_L$, and transverse wave velocities, $V_T$.

These parameters are determined from the combination of the following relations [12], [13]:

\[ E/G = 2.587 \]  
\[ G = \rho V_T^2 \]  
\[ E = G (3V_L^2 - 4V_T^2)/(V_I^2 - V_T^2) = \rho V_T^2 (3V_L^2 - 4V_T^2)/(V_I^2 - V_T^2) \]  
\[ B = \rho (V_I^2 - 3/4 V_T^2) \]  
\[ \nu = E/(2(\rho V_T^2) - 1) \]

where $\rho$ is the density of bulk ZnO ($\rho_{\text{ZnO}} = 5605$ kg/m$^3$ [14]).

(d) Acoustic Microscopy Computing Procedure: SAM, a non-destructive technique, is based on the determination of acoustic signatures, known as $V(z)$, which are the most important quantitative quantity, can be measured experimentally by recording the output voltage, $V$, at the piezoelectric transducer when the distance $z$ between the
lens and the sample surface varies or computed via different corresponding physical models [6], [7], [15]. The computing procedure, for every NW, consists of several steps:

(i) Introducing the above deduced velocities \( V_L \) and \( V_T \) into a simulation program under conventional conditions of a SAM: a lens half-opening angle of 50°, a frequency of 142 MHz, and a Freon couplant with \( V_{liq} = 716 \text{ m/s} \) and \( \rho_{liq} = 1.57 \text{ g/cm}^3 \).

(ii) Calculating reflection coefficients, \( R(\theta) \), for every liquid/ZnO NW combination, where \( R(\theta) \) is a complex function admitting a modulus \( |R| \) and a phase \( \phi \), given by [16]-[18]:

\[
R(\theta) = \left( Z_{sol} - Z_{liq} \right) / \left( Z_{sol} + Z_{liq} \right)
\]

with liquid impedance: \( Z_{liq} = \rho_{liq} V_{liq} \cos \theta \) (where \( \rho_{liq} \) and \( V_{liq} \) are the velocity and the density in the coupling liquid, respectively) and solid impedance: \( Z_{sol} = Z_L \cos^2 (2\theta_L) + Z_T \sin^2 (2\theta_T) \) (where \( Z_L \), \( Z_T \) are the longitudinal and transverse impedances and \( \theta_L \), \( \theta_T \) are the longitudinal and transverse critical angles).

(iii) Deducing of \( V(z) \) curves from:

\[
V(z) = \int \left[ P^2(\theta) R(\theta) \exp(2jk_{m}z\cos\theta) \sin\theta \cos\theta d\theta \right]
\]

where \( P^2(\theta) \) is the pupil function, \( \theta \) is the half-opening angle of the lens, \( z \) is the defocusing distance, and \( k_m = 2\pi / \lambda \) is the wave number in the coupling liquid, \( j = \sqrt{-1} \).

(iv) Applying fast Fourier transform (FFT) to the treatment of periodic \( V(z) \) to deduce Rayleigh velocity, \( V_R \), from the principal peaks of FFT spectra according to [16]:

\[
V_R = V_{liq} \sqrt{1 - (1 - V_{liq}^2 / 2\Delta Z)}^2
\]

where, \( f \) is the operating frequency.

(e) Determination of \( A = f(D_{wire}) \) expression: The \( A-D_{wire} \) relation is determined with \( A \) representing \((E, G, B, V_L, V_T, V_R, \theta_L, \theta_T, \theta_R)\).

III. RESULTS AND DISCUSSION

A. Influence of ZnO NW Diameters on Young’s Modulus

To quantify the nanomechanical behavior of ZnO NWs (with \( D_{wire} \leq 400 \text{ nm} \)) oriented along the [0001] direction, we consider some data reported by different theoretical and experimental methods under different loading modes (tension, buckling, and resonance). The obtained results are shown in Fig. 1, where the Young’s modulus (E) is presented as a function of the diameter \( (D_{wire}) \).

Different used methods are classified by the following: (i) computational Molecular Dynamics method (MD) via empirical Buckingham-type potential with Tension loading mode [3], [8] and (ii) experimental methods of Micromechanical system (MEMS) with Tension [3], Contact resonance Atomic Force Microscopy (CR-AFM) [9], Nanoindentation-Transmission Electron Microscopy (NI-TEM) [5]. Scanning Electron Microscopy (SEM) with Tension [10], SEM with Buckling [10], and AFM Cantilever in situ SEM with Tension [11]. The horizontal dashed line represents the corresponding bulk value along the [0001] direction [4].

It is clear that the general trend of the E-\( D_{wire} \) curves obtained by all methods is characterized by a rapid initial decrease for small diameters \( (D_{wire} \leq 100 \text{ nm}) \) followed by a tendency towards saturation for higher diameters \( (100 \text{ nm} \leq D_{wire} \leq 400 \text{ nm}) \). The E-\( D_{wire} \) behavior in initial decreasing region can be expressed by an exponential dependence obtained via curve fitting (plotted as solid line):

\[
E = 127 + 75.37 \exp(-D_{wire}/58.38)
\]

We notice that the mechanical behavior of ZnO changes from that of NWs to bulk material at the critical diameter \( (D_{wire} = 100 \text{ nm}) \) for which \( (E_{wire} \approx E_{bulk} = 140 \text{ GPa}) \).

B. Influence of ZnO NW Diameters on Elastic Parameters

<table>
<thead>
<tr>
<th>TABLE I</th>
<th>ELASTIC CONSTANTS AND WAVE VELOCITIES ARE CALCULATED IN BOTH NWs AND BULK ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_{wire} ) (nm)</td>
<td>( E ) (GPa)</td>
</tr>
<tr>
<td>1</td>
<td>201.09</td>
</tr>
<tr>
<td>10</td>
<td>190.50</td>
</tr>
<tr>
<td>20</td>
<td>180.51</td>
</tr>
<tr>
<td>30</td>
<td>172.08</td>
</tr>
<tr>
<td>40</td>
<td>164.99</td>
</tr>
<tr>
<td>50</td>
<td>159.00</td>
</tr>
<tr>
<td>60</td>
<td>153.97</td>
</tr>
<tr>
<td>70</td>
<td>149.72</td>
</tr>
<tr>
<td>80</td>
<td>146.15</td>
</tr>
<tr>
<td>90</td>
<td>143.13</td>
</tr>
<tr>
<td>100</td>
<td>140.59</td>
</tr>
<tr>
<td>Bulk</td>
<td>140.00</td>
</tr>
</tbody>
</table>
To study the influence of nano-diameters on elastic constants and wave velocities (E, G, B, v, V_L, and V_T) of ZnO NWs, we must focus on the previously deduced relation (9) as well as (1)-(5). Several D_wire values were chosen from 1 to 100 nm with a step of 10. The results, thus obtained, are shown in Table I.

It is clear that, whenever the wire diameters increase, the elastic parameters decrease till they reach bulk values, confirming the dependence of elastic properties with the size for D_wire ≤ 100 nm.

### C. Influence of ZnO NW Diameters on R(θ) and V(z) Curves

To illustrate the influence of ZnO wire diameter on reflection coefficient and acoustic signatures, we plot in Fig. 2 typical results (D_wire = 10 nm, 30 nm, 50 nm, 70 nm, and 90 nm) of the variation of R(θ) in terms of amplitude (dashed line referred to the left hand side) and phase (solid line referred to the right-hand side) as a function of incident angles, θi (Fig. 2(a)) and V(z) curves with FFT spectra (Fig. 2(b)). It is obvious that:

(i) For all NWs, the amplitude of R(θ) curves (Fig. 2(a)) has similar behavior (a saturation, a sharp peak, another saturation, a smooth increase and a final saturation with |R| = 1). The first fluctuation corresponds to the excitation longitudinal waves at critical angles, θL, and the second in amplitude corresponds to the excitation transverse waves at critical angles, θT.

(ii) The displacement of critical angles (θL, and θT) gradually becomes high when D_wire increases from 10 to 90 nm.

(iii) All the curves dealing with the phase show a large fluctuation of 2π around the Rayleigh-wave critical angle, θR. The θR fluctuations increase from 12.50° to 14.60° as the diameters increase from 10 to 90 nm.

(iv) All the acoustic signatures curves, in Fig. 2(b), exhibit a series of regular periodical oscillations, Δ(z), between two successive maxima or minima. These oscillations are due to the interference between two acoustical components detected by the transducer [6], [7], [16].

(i) As D_wire increases, we notice a change in V(z) amplitudes as well as in Δ(z).

(ii) The spectral analysis of V(z) curves is carried out via FFT treatment. The periods Δz are closely related to the SAW velocities of the material studied. Hence, each principal ray corresponds to the velocity of a given mode [6], [7], [16]. The analysis of the FFT spectra confirms the decreasing of velocity of longitudinal and Rayleigh modes with increasing D_wire. As D_wire change from 10 to 90 nm, V_L decreases from 6704 to 5811 m/s and V_R from 3371 to 2922 m/s.

(iii) At D_wire = 90 nm, the critical angles (θL, θT, θR), the V(z) signatures, and the wave velocities (V_L, V_T, and V_R) of NWs approach the values of their analogous bulk values.

### D. Quantification of Nanomechanical Behavior

To enhance the present work and validate the above results that were obtained from E-D_wire (9), we plot the calculated results of shear modulus, G, bulk modulus, B, and velocities: V_L, V_T, and V_R at different values of D_wire. Some typical results are depicted in Fig. 3. The general tendency is for a decrease in G, B, V_L, V_T, and V_R as ZnO wire diameters increase. Using a simple fitting procedure, it is possible to find exponential dependence (black solid line) of the form:

\[ G = 49.08 + 29.15 \exp(-D_{wire}/58.43) \]  
\[ B = 102.69 + 60.64 \exp(-D_{wire}/58.04) \]
\[ V_L = 5437.97 + 1473.84 \exp(-D_{wire}/65.57) \]
\[ V_T = 2937.83 + 798.96 \exp(-D_{wire}/65.88) \]
\[ V_R = 2732.63 + 742.91 \exp(-D_{wire}/65.85) \]

All these relations of similar exponential forms can be expressed as:

\[ A = a + b \exp(-D_{wire}/c) \]  

where a, b, and c are the characteristic constants deduced for each parameter; the values of these constants are regrouped in Table II.

The advantage of the present equation lies in the possibility of evaluating the elastic properties based on the NW diameter (as shown in our previous works [13], [19], [20]). This would be useful for experimental synthesis and technological applications by designing such ZnO wire with desired properties to achieve the adequate elasticity which is highly required for good reliability and high performance of nanoscale devices.

It is worth noting that the ZnO NWs are likely to behave as bulk ZnO for D_wire ≥ 100 nm whose E = 140 GPa, G = 54.12 GPa, B = 112.95 GPa, V_L = 5747 m/s, V_T = 3107 m/s and V_R = 2890 m/s.

### Table II

<table>
<thead>
<tr>
<th>Const</th>
<th>E</th>
<th>G</th>
<th>B</th>
<th>V_L</th>
<th>V_T</th>
<th>V_R</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
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<tr>
<td></td>
<td>127</td>
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<td>102.69</td>
<td>5437.97</td>
<td>2937.83</td>
<td>2732.63</td>
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<td>103.11</td>
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</table>

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Fig. 2 Effects of ZnO wire diameters, 1 nm ≤ D_{wire} ≤ 90 nm, on (a) R(θ) modulus (dashed line) and phase (solid line) and (b) V(z) with their FFT spectra. The lowest curves represent those of bulk ZnO, for comparison.
Fig. 3 Effects of ZnO wire diameters ($D_{wire}$ ≤ 400 nm) on (a) elastic constants: $E$ ($\Box$), $B$ ($\bigcirc$) and $G$ ($\Delta$) and (b) velocities: $V_L$ ($\Box$), $V_T$ ($\bigcirc$) and $V_R$ ($\Delta$). The horizontal dashed lines represent the corresponding calculated bulk value along the [0001] direction.

### IV. CONCLUSION

The effects of ZnO NWs diameters ($D_{wire}$ ≤ 400 nm) on Young’s modulus have been investigated and extended to other acoustic parameters. It was found that, for increasing wire diameters, all the curves show two distinct behaviors: an initial decrease followed by a saturation region that begins at $D_{wire} = 100$ nm corresponding to bulk materials values. The quantification of the initial decreasing region was found to have an exponential behavior of the form $A = a + b \exp(-D_{wire}/c)$ where $a$, $b$, and $c$ are characteristic constants. Thus, the importance of such formula lies in the prediction of elastic-acoustic properties of ZnO NWs through control of wire diameters and vice versa.

### REFERENCES