Structure dependence of piezoelectric size effects and macroscopic polarization in ZnO nanowires: A first principles study

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Axial effective piezoelectric coefficient of ZnO nanowire increases as the size decreases, and the increase mainly comes from the change in volume per ZnO pair with strain.

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Structure Dependence of Piezoelectric Size Effects and Macroscopic Polarization in ZnO Nanowires: A First Principles Study

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ABSTRACT
Piezoelectric properties of [0001] ZnO nanowires are investigated via density functional theory (DFT). Axial effective piezoelectric coefficient of ZnO nanowire is remarkably larger than bulk value, and the nanowire’s coefficient increases as the size decreases. It is proved that the enhancement in nanowires comes from both the reduction of volume per Zn-O pair and the enhancement of Poisson ratio. Further study shows that the macroscopic polarization behavior of ZnO nanowires is determined by the crystal structure parameters and surface atoms ratio, and an analytic expression has been obtained. This work helps to gain a deep understanding of the size effects of the piezoelectricity of ZnO nanowires and shed some light on the confusion reported on this subject.

1 Introduction
Materials with non-central-symmetry structures produce inside electrostatic potentials when subjected to external strains, which leads to piezoelectricity. Most recently, there is an increasing interest in ZnO piezoelectric nano-devices, such as piezoelectric field effect transistors [1], piezoelectric vibration sensors [2] and piezoelectric generators [3, 4]. The photoresponse with piezoelectricity of Cu₂O/ZnO heterojunction [5] was also studied as Z.L. Wang introduced the concept of piezo-phototronics combining the piezoelectricity and optoelectronics [6]. Piezoelectric nanostructures show their distinctions for three reasons: external mechanical energy is usually sufficient to actuate small piezoelectric materials [7]; it’s fairly easy to prepare mono-crystal nanostructures [8, 9] which don’t failure [10] with applied high strains and high electric fields; novel properties such as quantum effects [11], interfacial
effects [12], and size effects [13] will become observable when it comes to nano scale. On the theoretical frontiers, first principles studies about piezoelectricity of bulk ZnO [14] have been proved to be sound, and recent studies are very detailed about methodologies [15]. However, only a handful of theoretical investigations on ZnO nanowires have been carried out, and the obtained results don’t reach a conformity especially in terms of size effects. Li [16] revealed that the effective elastic constants $C_{33}$ of ZnO nanowire decreases drastically while the cohesive energy increases as the diameter decreases. Xiang [17] presented that the effective piezoelectric coefficients of ZnO nanowires with diameters from 0.6 nm to 2.8 nm are about 26-39% higher than the bulk value. Agrawal [18] suggested giant piezoelectric size effects: nearly 2 orders of magnitude enhancement can be attained if the diameter is reduced to less than 1 nm. But Cicero [19, 20] claimed that the core region’s effective piezoelectric coefficients nanowires are 1.19 Cm$^{-2}$ and 1.21 Cm$^{-2}$, very close to the bulk value 1.28 Cm$^{-2}$ [14]. There are two causes responsible for the above inconformity. The first one is their different definitions of nanowire’s effective piezoelectric coefficient in previous works, as the conventional definition of piezoelectric coefficient for bulk materials is not appropriate for characterizing the piezoelectricity of nano materials [17]. The other cause lies in the method to calculate the volume of a nanowire, which is very crucial to the coefficient of thin nanowires. By considering the atoms as point charges or finite spheres, one may obtain a dramatic uncertainty in the volume (nearly 70% in the case of the smallest nanowire) [20], which leads to a large deviation on the coefficient depending on the dipole moment per unit volume.

In this paper, density functional theory (DFT) was employed to study the piezoelectric properties of [0001] oriented ZnO nanowires. Our new method to evaluate the volume of nanowires was proposed, as in previous works the volume was a major source of confusion in the evaluation of piezoelectricity. The calculated nanowire’s effective piezoelectric coefficient is found to increase as the diameter decreases, and both of ZnO nanowire’s average volume per Zn-O pair and the change of volume with strain are found to play the key role of the observed size effects. The structure dependence of macroscopic polarization is further studied and it can be expressed by an analytical formula.

## 2 Computational Methods

DFT calculations were performed using the SIESTA [21] code. Generalized gradient approximation in the form of Perdew-Burke-Ernzerhof (GGA-PBE) was adopted for the exchange correlation functional and double-$\zeta$ polarization (DZP) numerical atomic-orbitals were chosen as basis sets. Norm-conserving pseudopotentials were generated from the Troullier-Martins scheme [22] with core-valence interactions in our calculations. Mesh cutoff was 400 Ry, and the force tolerance on each atom was less than 0.02 eVÅ$^{-1}$. 1$\times$1$\times$9 Monkhorst-Pack grids were chosen after convergence study. Piezoelectric properties were evaluated utilizing the Berry Phase [23, 24] method. Hexagonal supercells were adopted with the same c axis and large lateral distance between the periodic nanowires. After geometry relaxation, the cross sections of the ZnO nanowires are shown in Fig. 1(a).

We call them sample A, B, C, with diameters of about 0.6 nm, 1.2 nm, 1.8 nm.

Regarding the complicated atomic movements in a nanowire under stress, it is hard to study the piezoelectric coefficient $e_{33}$. The pragmatic effective piezoelectric coefficient $e_{33}^{eff}$ is defined as reported in previous works [18]

$$ e_{33}^{eff} = \partial P_3 / \partial \varepsilon_\parallel - \partial (p_3 / V) P_3 / \partial \varepsilon_\parallel $$  \hspace{1cm} (1)

where $P_3$ and $p_3$ are the macroscopic polarization and dipole moment along the axial direction, and strain $\varepsilon_\parallel$ is defined as the change ratio of lattice constant $c$, and $V$ represents the volume of certain structure. Volume occupied by certain ZnO atoms in the bulk is a well-defined quantity, and the volume of
Figure 1 (a) Cross sections of relaxed ZnO nanowires with different sizes. (b) Schematic diagram illustrating the method used to estimate the cross sectional area of nanowire B. The cross-section area is specified by a hexagon with black edge, and the length L and l are indicated in the figure.

nanowires can be made in a similar way. A rigid hexagonal zinc oxide nanowire can be abstracted in the perfect wurtzite crystal as shown in Fig. 1(b), where the unrelaxed nanowire B is located by a regular hexagon, and the unrelaxed nanowire’s constitutive volume per supercell can be defined as:

\[ V = S, \]

where \( S \) is the cross sectional area, and \( c \) is the lattice constant of the supercell. From the cross section view, six edges of the hexagon cut the Zn-O bonds at the middle and that correctly accounts the volume. Therefore, \( S \) for nanowire can be obtained by figuring out the area of the black regular hexagon as shown in Fig. 1(b). The longest length \( L \) within the supercell along the \( a \) axis can be used to calculate the edge length of the hexagon \( l \):

\[ l = \frac{n}{2(n-1)}L \]

(3)

where \( n \) is the shell number of a nanowire. Thus the nanowire’s volume per supercell can be presented as:

\[ V = Sc = \left(\frac{3\sqrt{3}}{2}\right)cL = \left(\frac{3\sqrt{3}}{2}\right)\left(\frac{n}{2(n-1)}\right)Lc \]

(4)

This formula can be generated to calculate the volume of relaxed ZnO nanowires. Since Zn atoms move inwards much more than O atoms after geometry relaxation, so the length \( L \) should be treated as the average value of Zn and O atoms. Another volume calculation method considering atoms as point charges is illustrated in the Fig. S1 (in the Electronic Supplementary Material (ESM)). As the electrons occupy most of the space in the material, it is unreasonable to treat atoms as point charges in the surface region. It will undervalue the volume of nanowire especially for nanowire A as shown in Fig. S2. Therefore, we choose the calculation method illustrated in Fig. 1(b).

3 Results and discussion

The calculated structural parameters and the piezoelectric coefficient \( e_{33} \) for ZnO bulk are shown in Table 1. Structural parameters are in good agreement with the experiment [25], and \( e_{33} \) is also close to that of previous work [14]. These results show that our modeling approaches and pseudopotentials for ZnO structures and piezoelectric properties are valid.

Geometry relaxations were performed for the ZnO nanowires without any strain and the structural parameters are listed in Table 2. It is clear that lattice

<table>
<thead>
<tr>
<th>sample</th>
<th>( L_0(\text{Å}) )</th>
<th>( L(\text{Å}) )</th>
<th>( V(\text{Å}^3) )</th>
<th>( c(\text{Å}) )</th>
<th>( u )</th>
<th>( \eta )</th>
<th>( \nu )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.249</td>
<td>2.979</td>
<td>20.648</td>
<td>5.375</td>
<td>0.341</td>
<td>1.00</td>
<td>0.474</td>
</tr>
<tr>
<td>B</td>
<td>9.747</td>
<td>9.201</td>
<td>21.600</td>
<td>5.302</td>
<td>0.345</td>
<td>0.75</td>
<td>0.412</td>
</tr>
<tr>
<td>C</td>
<td>16.245</td>
<td>15.685</td>
<td>22.454</td>
<td>5.269</td>
<td>0.358</td>
<td>0.56</td>
<td>0.376</td>
</tr>
<tr>
<td>bulk</td>
<td>23.861</td>
<td>5.220</td>
<td>0.380</td>
<td>0.00</td>
<td>0.337</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
constant $c$ increases and the volume per Zn-O pair decreases as the nanowire gets thin. The surface atoms displacement can be seen in Fig. 1(a) while atoms in the core region don’t move a lot. Lateral size obviously contracts as nanowire’s $L$ is smaller than the unrelaxed value $L_0$ in Table 2, because the energy of nanowire is higher than that of bulk as revealed in Li’s work [16]. To calculate the effective piezoelectric coefficients $e_{33}^{\text{eff}}$ of ZnO nanowires, a series of strains from -1% to 1% at an increment of 0.2% were applied along the c axis. The atomic coordinates were fully relaxed and the nanowire’s lateral size thus changes during the strain. It should be noted that one should not compare the nanowire’s $e_{33}^{\text{eff}}$ to the bulk’s $e_{33}$ to evaluate the size effects. And the lateral contraction or expansion during the strain must be taken into account in calculating the bulk $e_{33}^{\text{eff}}$. So the Poisson ratio of 0.337 for ZnO bulk was implemented as calculated in our previous work [26].

The macroscopic polarization along the [0001] direction was calculated and plotted in Fig. 2. It clearly reveals that at a given strain, the $P_3$ of any nanowire is remarkably larger than that of bulk, and a good linear correlation between the $P_3$ and the strain can be found. Here the macroscopic polarization is different from the conventional net polarization, which is a relative value to a reference system. But the macroscopic value is more general and brief, so we use it to clearly characterize the polarization feature of ZnO nanowires. The linear regression method was employed to get the slopes for nanowire A, B, C and the bulk respectively, and the slope is just right the $e_{33}^{\text{eff}}$ as defined in Eq. (1).

We listed the obtained coefficients in Table 3, together with some previous works. In the third column we have transformed the unit of effective piezoelectric coefficients into $\text{Cm}^{-2}$ in Xiang’s work [17] through our volume calculation methods in the paper’s second section.

The size effects here are similar to the result converted from Xiang’s work [17], but obviously not so giant as reported by Agrawal’s work [18], where the large deviation can be attributed to the methods (illustrated in Fig S1) used to evaluate the volume of ZnO nanowires. In Hoang’s [27] definition for effective piezoelectric coefficient, they fixed the value of volume and thus got the relatively small results. In the following part we will illustrate the importance of volume change during the strain. In our work, we can also see that the difference of $e_{33}^{\text{eff}}$ between nanowire C and bulk is not very large. Previous works [17, 18, 27] also reported the size effects of piezoelectric properties but without further explanations. In this section, detailed discussion about the contributions of volume and the macroscopic electric dipole moment to the size effects will be given. In order to make the comparison between different structures meaningful, the average macroscopic electric dipole moment $p_{3a}$ and average volume per Zn-O pair $V_a$ were used, and Eq. (1) can be written as

$$e_{33}^{\text{eff}} = \partial(p_3/V_a)/\partial V_a \partial \frac{\partial (p_{3a}/V_a)}{\partial \sigma}$$

$$= \left(\partial p_{3a}/\partial \varepsilon \right)_{V_a} V_a^{-1} + p_{3a}(\partial V_a^{-1}/\partial \sigma)$$

Thus both $p_{3a}$ and the reciprocal of average volume $V_a^{-1}$ as a function of strain determine the effective piezoelectric coefficient, and they are plotted as

![Figure 2](image)

**Figure 2** Macroscopic polarization along the c axis as a function of strain for relaxed ZnO nanowires and the bulk.

<table>
<thead>
<tr>
<th>sample</th>
<th>this work</th>
<th>Ref. [17]</th>
<th>Ref. [18]</th>
<th>Ref. [27]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>29.985</td>
<td>28.167</td>
<td>119.94</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>25.756</td>
<td>25.552</td>
<td>45.789</td>
<td>7.995</td>
</tr>
<tr>
<td>C</td>
<td>22.735</td>
<td>26.137</td>
<td>32.739</td>
<td>4.376</td>
</tr>
<tr>
<td>bulk</td>
<td>20.189</td>
<td>20.211</td>
<td>19.210</td>
<td>1.880</td>
</tr>
</tbody>
</table>

Table 3 The effective piezoelectric coefficient (Cm$^{-2}$) for different ZnO structures in our work and references.
functions of strain in Fig. 3. It’s clear that $p_{3A}$ increases with strain while decreases with diameter; $V_3^{-1}$ decreases with strain and diameter. But the bulk value of $p_{3A}$ is larger than that of any nanowire, which can also be found in previous work [18]. We will discuss more about $p_{3A}$ in the next subsection.

In order to figure out how $p_{3A}$ and $V_3^{-1}$ influence the effective piezoelectric coefficients, the numerical results of the variables in Eq. (5) are listed in Table 5.

It can be seen clearly that both $p_{3A}$ and $\partial p_{3A}/\partial \varepsilon_3$ change slightly with the size of nanowires while $V_3^{-1}$ and $\partial V_3^{-1}/\partial \varepsilon_3$ change obviously. The first term ($\partial p_{3A}/\partial \varepsilon_3)\partial V_3^{-1}$ changes from 31.42949 Cm$^{-2}$ for nanowire A to 26.79180 Cm$^{-2}$ for the bulk, and the second term $p_{3A}(\partial V_3^{-1}/\partial \varepsilon_3)$ changes from -1.44133 Cm$^{-2}$ for nanowire A to -6.60469 Cm$^{-2}$ for the bulk. In previous works, it can also be drawn that the volume reduction of nanowire causes the enhancement in $e_{33}^{eff}$ with respect to bulk crystal. Fig. 5 reveals that the unreasonable method for volume calculation lead to very large effective piezoelectric coefficients especially for nanowire A. Due to this method which leads to remarkably small value of average volume for thin nanowires, the obtained coefficients in Agrawal’s work [18] are very large. What’s more, this work further demonstrates that the change of average volume during the strain reduces the $e_{33}^{eff}$. Ignoring the change of volume will surely underestimate the coefficients as in Hoang’s work [27]. Therefore, both the reduction of average volume and the change of average volume with strain played almost equally important roles in size effects of piezoelectricity.

A very brief modulus determining the term $\partial V_3^{-1}/\partial \varepsilon_3$ is the Poisson ratio $\nu$. A higher $\nu$ means a higher $\partial V_3^{-1}/\partial \varepsilon_3$, which can be clearly found through data in Table 2 and Table 4. Therefore, it’s noteworthy that recent works have showed extensively dispersed Poisson ratios for various ZnO materials. Pant [28] characterized the structure of epitaxial ZnO films through a two-step growth method at series of low

![Figure 3](image.png)

**Figure 3** (a) $p_{3A}$ as a function of strain for relaxed ZnO nanowires. (b) $V_3^{-1}$ as a function of strain for relaxed ZnO nanowires.

**Table 4** The value of variables in Eq. (5) for ZnO nanowires and bulk.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\partial p_{3A}/\partial \varepsilon_3$ (eBohr)</th>
<th>$V_3^{-1}$ (Å$^3$)</th>
<th>$(\partial p_{3A}/\partial \varepsilon_3)V_3^{-1}$ (Cm$^{-2}$)</th>
<th>$p_{3A}$ (eBohr)</th>
<th>$\partial V_3^{-1}/\partial \varepsilon_3$ (Å$^3$)</th>
<th>$\partial p_{3A}(\partial V_3^{-1}/\partial \varepsilon_3)$ (Cm$^{-2}$)</th>
<th>$e_{33}^{eff}$ (Cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>76.544</td>
<td>0.04843</td>
<td>31.42949</td>
<td>71.231</td>
<td>-0.00239</td>
<td>-1.44133</td>
<td>29.986</td>
</tr>
<tr>
<td>B</td>
<td>76.307</td>
<td>0.04587</td>
<td>29.6746</td>
<td>70.812</td>
<td>-0.00665</td>
<td>-3.99333</td>
<td>25.752</td>
</tr>
<tr>
<td>C</td>
<td>76.031</td>
<td>0.04412</td>
<td>28.43661</td>
<td>70.662</td>
<td>-0.00974</td>
<td>-5.83315</td>
<td>22.733</td>
</tr>
<tr>
<td>Bulk</td>
<td>75.389</td>
<td>0.04191</td>
<td>26.79180</td>
<td>71.421</td>
<td>-0.01090</td>
<td>-6.60469</td>
<td>20.187</td>
</tr>
</tbody>
</table>
temperatures, which leads to abnormal Poisson ratios ranging from 0.08 to 0.54. For single-walled ZnO nanotubes, Mirnezhad [29] has demonstrated a changing values from 0.2 to 0.61 with different patterns of hydrogen adsorption. Qing [30] has also obtained a high Poisson ratio of 0.667 for graphene-like hexagonal ZnO monolayer. So attention of Poisson ratio may be helpful for piezoelectricity investigation in ZnO nanomaterials. After studying the size dependence of piezoelectricity for ZnO nanowires, we proceed to further study the polarization mechanism of ZnO nanowires along [0001] direction. Since distinguished works about polarization in bulk ZnO and some localized features have been reported, we’ll have more attention on the structure dependence of macroscopic polarization. The change in average macroscopic dipole moment can be related to three major factors: (i) lattice constant of \( c \), (ii) fractional coordinate of \( u \), (iii) ratio of surface atoms \( \eta \). The above parameters were calculated and listed in Table 2. Therefore, the average dipole moment \( p_{3a} \) may be expressed as

\[
p_{3a} = f(c,u) + h_{\text{surf}}(\eta) + p_{3a}^0
\]

where \( f(c,u) \) and \( h_{\text{surf}}(\eta) \) account for the contributions of crystal structure and surface effect respectively, and \( p_{3a}^0 \) is a constant value.

In order to study the effect of each parameter, further DFT calculations were performed on unrelaxed nanowires with series values of \( c \) and \( u \). Values of \( p_{3a} \) as functions of \( c \) and \( u \) are plotted in Fig. 4(a) and (b) respectively. It can be found that the increase of \( c \) or decrease of \( u \) can lead to a higher \( p_{3a} \). Fig. 4 demonstrates very good linear correlations between \( p_{3a} \) and \( c, u \) for ZnO nanowires. The slopes for each set of data in Fig. 4 were evaluated and listed in Table 5. Values of \( \partial p_{3a}/\partial c \) for different nanowires, in other words different surface atoms ratios, are almost the same, which supports the rationality to split up the contributions of structure relaxation and surface ratio in Eq. (6). Therefore, approximately we choose that \( \partial p_{3a}(c,u,\eta)/\partial c = \partial f(c,u)/\partial c = I_c = 7.726 \text{ e} \) to evaluate the contribution of \( c \). Similarly, we have \( \partial p_{3a}(c,u,\eta)/\partial u = \partial f(c,u)/\partial u = I_u = -22.89 \text{ eBohr} \). From the above results, we make a statement about the effect of structure on the polarization of ZnO: large \( c \) or small \( u \) will lead to large \( p_{3a} \) with a linear correlation.

To deliberate the underlined physics, let’s discuss the subject further. Since the value of macroscopic electric dipole moment can be simply obtained as the product of charge and distance between the ions, it is easily found that the enhancement of \( c \) will surely increase \( p_{3a} \). In a simple picture, assume a linear relationship between \( p_{3a} \) and \( c \), then \( \partial p_{3a}/\partial c = p_{3a}/c \). The estimated \( p_{3a}/c \) values are also listed in Table 5 behind the \( \partial p_{3a}/\partial c \) column for easy comparison. It can be seen that the values in the two columns are close and that the deviation is relatively larger for ZnO

![Figure 4](image-url) (a) Averaged macroscopic electric dipole moment as a function of lattice constant \( c \) for unrelaxed ZnO nanowires and the bulk.

(b) Averaged macroscopic electric dipole moment as a function of fractional coordinate \( u \) for unrelaxed ZnO nanowires and the bulk.
nanowire A. This indicates that the effect of $c$ on $p_{3a}$ is mainly attributed to the displacement of ions in the unit cell.

At the same time, the increment of $u$ means that the O atoms plane moves closer to the Zn atoms plane, so that the polarization along the $c$ direction is weakened which leads to a lower $p_{3a}$. In a simple picture, O and Zn ions assume formal charge $q$ (2e for Zn and -2e for O ion), and the displacement of the ions center can be estimated as $-cduc$. So the change in $p_{3a}$ with $u$ can be calculated according to $\partial p_{3a}/\partial u = -qec$. The $\partial p_{3a}/\partial u$ values calculated from first principle calculation and the estimated $-qec$ values are listed in Table 5 for comparison. One should note that the unrelaxed structures share the same $c$, and thus the same $-qec$. It can be seen that the values of $\partial p_{3a}/\partial u$ and $-qec$ are quite close. This is why the macroscopic dipole moment is a very general quantity in condensed matter and we pay more attention on it.

For the fully relaxed nanowires, which show higher values of $c$ and lower values of $u$ than that of the bulk ZnO (which can be found in Table 2), the relaxed crystal structure lead to higher value of $p_{3a}$ than the unrelaxed ones. So the structure relaxation is to some extend a compensation for polarization reduction.

In order to study the surface effect, the average macroscopic dipole moment along the $c$ axis ($p_{3a}$) as a function of surface ratio ($\eta$) for relaxed and unrelaxed ZnO nanowires and the bulk without strain are plotted in Fig. 5. A linear correlation between the $p_{3a}$ and $\eta$ can be seen clearly for the unrelaxed ZnO nanowires. As the nanowire grows thicker, surface atoms ratio decreases, and $p_{3a}$ increases. Therefore, we have

\[ h_{sat}(\eta) = \gamma_s \eta \]  

Figure 5 Average macroscopic electric dipole moment along the $c$ axis as a function of surface ratio for relaxed and unrelaxed ZnO nanowires and the bulk without strain. The light green and blue curves are the linear and formula fits of the unrelaxed and relaxed nanowires, respectively.

where $\gamma_s$ is a constant value ($\gamma_s = -3.353$ eBohr). Therefore, the average dipole moment of the unrelaxed nanowire is linearly dependent on the surface atoms ratio. From the negative value of $\gamma_s$, it can be concluded that surface atoms contribute less than the core atoms. This is due to the redistribution of charge among the core and surface ions, and the dangling bonds in the surface area impair the polarization behavior. Thus the corresponding average dipole moment of every Zn-O pair at surface is lower than that of the core region or bulk. Explanation about why the average dipole moment for nanowires is smaller than that of bulk was also presented in Agrawal’s work [18] in terms of Mulliken charges. They found that the surface Zn-O pair shows a noticeable decrease of

Table 5 Values of $p_{3a}$, $\partial p_{3a}/\partial c$, $p_{3a}/c$, $\partial p_{3a}/\partial u$ and $-qc$ for the unrelaxed ZnO nanowires and bulk.

<table>
<thead>
<tr>
<th>sample</th>
<th>$p_{3a}$ (eBohr)</th>
<th>$\partial p_{3a}/\partial c$ (eBohr/Å)</th>
<th>$p_{3a}/c$ (eBohr/Å)</th>
<th>$\partial p_{3a}/\partial u$ (eBohr/Å)</th>
<th>$-qc$ (eBohr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>68.068</td>
<td>14.60</td>
<td>12.66</td>
<td>-22.89</td>
<td>-20.32</td>
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<tr>
<td>B</td>
<td>68.898</td>
<td>14.55</td>
<td>12.99</td>
<td>-21.77</td>
<td>-20.05</td>
</tr>
<tr>
<td>C</td>
<td>69.538</td>
<td>14.50</td>
<td>13.20</td>
<td>-21.02</td>
<td>-19.92</td>
</tr>
<tr>
<td>bulk</td>
<td>71.421</td>
<td>14.45</td>
<td>13.68</td>
<td>-20.49</td>
<td>-19.74</td>
</tr>
</tbody>
</table>
dipole moment with respect to the bulk value. Moreover, Hoang’s work [27] also revealed that the surface will significantly impair the piezoelectric behavior along the $c$ axis through the continuum slab model. Finally, the average macroscopic dipole moment $p_{3a}$ can be written as:

$$p_{3a}(c,u,\eta) = I_c(c - u_c) + I_u(u - u_u) + p^0_3$$ (8)

Now it’s clear that $p^0_3$ represents the average macroscopic dipole moment of the bulk, which shows no surface atoms ratio ($\eta = 0$). For a fully relaxed nanowire, Eq. (8) can be used to evaluate $p_{3a}$ with crystal structure parameters and surface ratio. The blue triangles in Fig. 5 represent the DFT calculated results while light blue curve shows the results of Eq. (8) and it can be found that the matches are quite well. Good matches also show that the average macroscopic dipole moment along the [0001] direction can be barely influenced by lateral structural relaxation, which is not included in Eq. (8). The values of surface atoms ratio of experimentally prepared ZnO nanowires are very close to 0, but the nanowires may have observable different structure parameters due to various conditions. Thus the above representation allows us to possibly extrapolate the macroscopic polarization in ZnO nanostructures.

Conclusion

To summarize, first-principles calculations were carried out to study the piezoelectric and polarization features of ZnO nanowires along the $c$ axis and their size effects. The effective piezoelectric coefficient of nanowire is larger than the bulk value and it increases markedly as the diameter decreases. In particular, the explanations about piezoelectric size effects have been elaborated, and both of the average volume per Zn-O pair in nanowires and its change rate with strain play the key role. Furthermore, theoretical predictions indicate that the polarization behaviors of ZnO nanowire mainly depend on two contributions, one related to the crystal parameters (including lattice constant $c$ and fractional coordinate $u$) and the other due to surface atoms ratio. Also an analytical expression to describe the macroscopic average dipole moment has been obtained using structural variables. Our work has established integrated methodology for investigating piezoelectricity and polarization properties in ZnO nanowires and these methods can be used to predict the piezoelectricity and polarization properties of wurtzite structured nanowires, such as GaN, AlN, etc.

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References


Electronic Supplementary Material

Structure Dependence of Piezoelectric Size Effects and Macroscopic Polarization in ZnO Nanowires: A First Principles Study

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Figure S1 Schematic diagram illustrating Agrawal’s method [18] used to estimate the cross sectional area of nanowire A. The cross-section area is specified by a hexagon with black edge.

Figure S2 (a) Average volume as a function of surface atoms ratio calculated by our method and that in the reference. (b) The effective piezoelectric coefficient as a function of surface atoms ratio through our volume calculation method and the method in the reference.
In order to explain the confusion caused by volume calculation method in piezoelectric size effects, we demonstrate the volume calculation method considering the atoms as point charges as reported in Ref.[18] in Fig S1. Fig S2 shows the comparison for the average volume and effective piezoelectric coefficient obtained by the two volume calculation methods.

It can be seen that the calculation of volume for thin nanowire should take into account the space occupied by electrons, and the key issue is the definition of boundary of the nanowires. Our scheme for volume calculation described in the paper is a facile and accurate one.