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First-principles based multiscale model of piezoelectric nanowires with surface effects

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A continuum model of nanowires incorporating surface piezoelectricity is proposed which extends the electric enthalpy energy with surface terms. The corresponding equations are solved by a numerical method using finite elements technique. A methodology is introduced to compute the surface piezoelectric coefficients by first-principles calculations through the Berry phase theory. We provide the $e_{33s}$, $e_{51s}$, and $e_{15s}$ piezoelectric coefficients of (10$ar{1}$0) surfaces for hexagonal wurtzite nanowires made of GaN, ZnO and AlN. The effective piezoelectric coefficient along the axis of the nanowire is found to increase when the diameter decreases, for the three studied materials. Finally, the solution of the continuum model is compared with large-size first-principles calculations on piezoelectric nanowires.

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I. INTRODUCTION

Recent experimental studies have evidenced higher performances of piezoelectric nanostructures as compared to bulk materials. Very recently, Qi and M. C. McAlpine have developed Pb-Zr-Ti (PZT) ceramics nanowires on a polymer and have reported the highest piezoelectric performance. These structures have then attracted a tremendous attention due to potential applications in energy harvesting, sensors, piezoelectric output voltage scale and self-powered nanodevices, among many others.

Piezoelectric coefficients $e_{33}$ and $e_{31}$ of nanowires can be measured by PFM (Piezoresponse Force Microscopy) and AFM tip-4 (Atomic Force Microscope). Espinosa et al. showed that a giant piezoelectric constant is observed in GaN and ZnO nanowires with very small diameters (about 2.5 nm for GaN nanowires). Another important aspect is the wide band gap of semi-conducting nanowires, which is influenced by surface effects for small diameters.

In addition, numerical investigations involving first-principles calculations confirm these effects. Following Li et al., Dai et al. evaluated the effects of surface piezoelectricity on ZnO, SrTiO$_3$ and BaTiO$_3$ systems by using first-principles and core-shell interatomic simulations.

In this paper, we propose a continuum model of piezoelectric nanowires with surface effects. We extend to piezoelectricity an approach previously proposed for modeling mechanical surface effects in nanowires. A procedure based on first-principles calculations is developed to compute the surface piezoelectric coefficients using slab surface models. A finite element methodology is used to solve the equations of the continuum model for a geometry involving a hexagonal section, corresponding to wurtzite monocystal nanowires made of GaN, AlN and ZnO. We then compare the values of the effective $e_{33}$ coefficient obtained by our model with full first-principles calculations on several nanowires with different diameters to assess the accuracy of the model.

II. CONTINUUM MODEL FOR SURFACE PIEZOELECTRICITY

Piezoelectricity is due to the atomic scale polarization (see a review of electromechanical phenomena in semiconductor nanostructures in reference). It is caused by the non centrosymmetric crystal structure of certain materials, which results in an effective change of polarization in response to an applied mechanical strain.

When considering surface effects in nanostructures, the total energy (enthalpy) of the system can be written as bulk and surface contributions:

$$ W = \int_{V} \omega^{b}(\varepsilon_{ij}, E_{i})dV + \int_{S} \omega^{s}(\varepsilon_{ij}^{s}, E_{i}^{s})dS $$

where $\omega^{b}$ and $\omega^{s}$ are the bulk enthalpy density and surface enthalpy density, respectively, while $\varepsilon$ and $E_{i}$ denote the strain second order tensor and the electric field vector. We assume the following forms for the energy (enthalpy) density functions:

$$ \omega^{b}(\varepsilon_{ij}, E_{i}) = \frac{1}{2} C_{ijkl} \varepsilon_{ij} \varepsilon_{kl} - e_{ijkl} E_{i} \varepsilon_{kl} - \frac{1}{2} \alpha_{ij} E_{i} E_{j} $$

and

$$ \omega^{s}(\varepsilon_{ij}^{s}, E_{i}^{s}) = \frac{1}{2} C_{ijkl}^{s} \varepsilon_{ij}^{s} \varepsilon_{kl}^{s} - e_{ijkl}^{s} E_{i}^{s} \varepsilon_{kl}^{s} - \frac{1}{2} \alpha_{ij}^{s} E_{i}^{s} E_{j}^{s} $$

$$ + \tau_{ij}^{s} \varepsilon_{ij}^{s} $$

where $C_{ijkl}$, $e_{ijkl}$, $\alpha_{ij}$ are the bulk elastic fourth-order tensor, the bulk piezoelectric third-order tensor and the bulk second-order dielectric tensor, respectively, while $C_{ijkl}^{s}$, $e_{ijkl}^{s}$, $\alpha_{ij}^{s}$ are their surface counterparts and $\tau_{ij}^{s}$ is the surface residual stress. These tensors have the following symmetries.
\[ C_{ijkl} = C_{klij} = C_{ijlk} = C_{jikl}, \]  
\[ e_{ijkl} = e_{klij}, \quad \alpha_{ijkl} = \alpha_{klji}. \]  

In Eq. (3), \( e^s \) and \( E^s \) are the surface strain tensor and surface electric field vector. In this work, the surface vectors \( v^s \) and second-order tensors \( A^s_{ij} \) are defined from their bulk definition through the use of an orthogonal projector operator \( T_{ij} = \delta_{ij} - n_i n_j \), describing the projection on the plane tangent to the surface \( S \) at \( x \in S \), where \( n_i \) is the unit vector normal to \( S \) at \( x \). Then, we have \( v^s = T_{ij} v_j \) and \( A^s_{ij} = T_{ik} A_{kl} T_{lj} \). The constitutive equations for bulk and surface can be established from (2)-(3) as

\[ \sigma_{ij} = \frac{\partial \omega^b}{\partial E_{ij}} = C_{ijkl} \varepsilon_{kl} - e_{ijkl} E_k, \]  
\[ D_i = \frac{\partial \omega^b}{\partial E_i} = e_{ikl} \varepsilon_{kl} + \alpha_{ik} E_k, \]  
\[ \sigma^s_{ij} = \frac{\partial \omega^s}{\partial E^s_{ij}} = C_{ijkl} \varepsilon^s_{kl} - e^s_{ijkl} E^s_k + \tau^s_{ij}, \]  
\[ D^s_i = -\frac{\partial \omega^s}{\partial E^s_i} = e^s_{ikl} \varepsilon^s_{kl} + \alpha^s_{ik} E^s_k \]  

where \( \sigma \) is the stress tensor and \( D \) the electric displacement. The polarization vector for bulk and surface, denoted by \( P \) and \( P^s \) respectively, are related to the electric displacement vectors by

\[ D_i = P_i + \epsilon_0 E_i, \quad D^s_i = P^s_i + \epsilon_0 E^s_i, \]  

where \( \epsilon_0 \) is the permittivity of vacuum. We can finally express the bulk and surface piezoelectric coefficients as

\[ e_{ijk} = \frac{\partial D_i}{\partial E_{jk}}, \quad e^s_{ijk} = \frac{\partial D^s_i}{\partial E^s_{jk}}, \quad \alpha_{ijkl} = \frac{\partial \sigma_{ij}}{\partial E_k}, \quad \alpha^s_{ijkl} = \frac{\partial \sigma^s_{ij}}{\partial E^s_k}. \]  

The effective polarization can be defined as

\[ P_i^{eff} = \frac{1}{V} \frac{\partial W}{\partial E_i^{eff}}, \]  

where \( E^{eff}_i \) denotes an effective electric field such that

\[ E_i^{eff} = \frac{1}{V} \int_V E_i dV. \]  

Then we have, using (1):

\[ P_i^{eff} = \frac{1}{V} \int_V \frac{\partial \omega^b}{\partial E_i^{eff}} dV + \frac{1}{V} \int_S \frac{\partial \omega^s}{\partial E_i^{eff}} dS \]  
\[ = \frac{1}{V} \int_V \frac{\partial \omega^b}{\partial E_j} \frac{\partial E_j}{\partial E_i^{eff}} dV + \frac{1}{V} \int_S \frac{\partial \omega^s}{\partial E_j} \frac{\partial E_j}{\partial E_i^{eff}} dS. \]  

From (13) we obtain

\[ \frac{\partial E_i^{eff}}{\partial E_i} = \frac{1}{V} \int_V \delta ij dV = \delta_{ij}. \]  

Furthermore, by noting that \( E_i^n = T_{ij} E_j \), it yields

\[ \frac{\partial E_i^{eff}}{\partial E_i} = T_{ik} \frac{\partial E_k}{\partial E_i^{eff}} = T_{ik} \delta_{kj} = T_{ij} \]  

and

\[ \frac{\partial \omega^s}{\partial E_i} \frac{\partial E_i^{eff}}{\partial E_i} = P^s_j T_{ij} = P^s_i. \]  

Thus, we finally obtain

\[ P_i^{eff} = \frac{1}{V} \int_V P_i dV + \frac{1}{V} \int_S P^s_i dS. \]  

The domain is subjected to Dirichlet boundary conditions, i.e. displacements and potential are prescribed over respective portions of the external boundary of the domain. To solve the problem, the total energy (1) of the system submitted to an applied external force \( F_i \) and external electric displacement \( D_i \), is expressed, in the absence of body forces by

\[ W = \int_{S_F} F_i u_i dS - \int_{S_D} \mathcal{T}_{i} n_i \phi dS, \]  

where \( S_F \) and \( S_D \) denote respectively the traction and electric displacement surfaces and \( \phi \) is the electric potential. The total energy expressed in (20) is optimized with respect to the nodal displacements and nodal electric potentials associated to a finite element mesh discretizing the domain \( \Omega \).

### III. FIRST-PRINCIPLES PIEZOELECTRIC CALCULATIONS

The calculations of the piezoelectric coefficients in the framework of periodic Density Functional Theory (DFT) were done using the Berry phase approach.\(^{35,36}\) In this
method, the piezoelectric coefficients $e_{ik}$ are obtained as:\cite{35}

$$e_{ik} = -\frac{1}{2\pi V} \sum_\alpha \frac{\partial \phi_\alpha}{\partial \epsilon_k} a_{\alpha i}, \quad (21)$$

where $V$ is the unit cell volume, the sum runs over unit cell directions, $a_\alpha$ being the corresponding unit cell vectors, and $\phi_\alpha$ the Berry phase in the direction $\alpha$, which is a sum of nuclear and electronic components,

$$\phi_\alpha = \phi_\alpha^{nuc} + \phi_\alpha^{elec} \quad (22)$$

with nuclear part as a simple geometric sum

$$\phi_\alpha^{nuc} = \sum_{iA} B_{\alpha i} R_{Ai} Z_A, \quad (23)$$

with the sum running over atoms in the unit cell $A$ and Cartesian components $i$, $B_{\alpha i}$ being reciprocal unit cell vectors, $R_{Ai}$ and $Z_A$ the coordinates and charges of the nuclei, respectively. The electronic part is evaluated by integrating over the Brillouin zone,

$$\phi_\alpha^{elec} = \frac{1}{\Omega} \sum_n \int_{BZ} \langle u_{nk} \rangle - i B_\alpha \nabla_k |u_{nk}| dk, \quad (24)$$

where $\Omega = (2\pi)^3/V$ is the Brillouin zone volume and the sum runs over all occupied orbitals in DFT wave function with $u_{nk}$ being the corresponding Bloch functions.

These total (nuclear and electronic) Berry phases are calculated by CRYSTAL09 code for a set of deformations (we used a total of 11 calculations for each distortion calculated by CRYSTAL09 code for a set of deformations with $\epsilon_{ik}$ sum runs over all occupied orbitals in DFT wave function where $\Omega = (2\pi)^3/V$).

The geometry is fully defined by the length of hexagonal edge $a$, the height $c$ of the prism, and by the relative distance $u$ between the two atoms of different type.

For a wurtzite crystal, the piezoelectric tensor has three independent components in Voigt’s notation $e_{33}$, $e_{31}$ and $e_{15} = e_{24}$: the first two components $e_{33}$, $e_{31}$ measure the variation of polarization along the axis 3 by a uniform strain in the plane normal to the 3-direction. The third constant $e_{15}$ describes the polarization induced by a shear strain perpendicularly to the axis 3. The matrix of bulk piezoelectric coefficients is then defined as follows

$$e = \begin{bmatrix} 0 & 0 & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{15} & 0 & 0 \\ e_{31} & e_{31} & e_{33} & 0 & 0 \end{bmatrix}. \quad (25)$$

The strain tensor is characterized in Voigt’s notation by the components $\epsilon = [\epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4, \epsilon_5, \epsilon_6]$. For wurtzite, the bulk elastic tensor can be expressed by five independent constants: $C_{11}$, $C_{12}$, $C_{13}$, $C_{33}$, and $C_{44}$ (see more details in).\cite{29,30,31} Bulk elastic parameters have been characterized in many other studies, including our previous papers.\cite{29,30,31} In this work, we have also computed the bulk piezoelectric coefficients for GaN, ZnO, and AlN by first-principles calculations in Table I for comparison with other studies. The bulk piezoelectric constants are given by:

$$e_{ik}^{ab} = \frac{1}{V_{cell}} \frac{\partial P_{ik}^{ab}}{\partial \epsilon_k}, \quad i = 1, 2, 3; k = 1, 2, ..., 6, \quad (26)$$

where $P_{ik}^{ab}$ is the total polarization per unit cell computed by first-principles calculations and $V_{cell}$ is the unit cell volume defined as:

$$V_{cell} = a^2 c \frac{\sqrt{3}}{2}. \quad (27)$$

The elastic constants have been evaluated at the atomistic level by first-principles calculations, through the CRYSTAL code,\cite{36} using the PBESOL and PWGGA DFT functionals. For GaN and AlN, the calculations with hybrid PBE0 were also performed. For bulk materials, we also give the B3LYP results. In the present work,
TABLE I: Bulk geometric (in Å) and elastic parameters (in GPa) for wurtzite GaN, ZnO and AlN.

<table>
<thead>
<tr>
<th>Method</th>
<th>a</th>
<th>c</th>
<th>C_{11}</th>
<th>C_{33}</th>
<th>C_{13}</th>
<th>C_{12}</th>
<th>C_{55}</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN</td>
<td>PWGGA</td>
<td>3.200</td>
<td>5.207</td>
<td>361.1</td>
<td>397.2</td>
<td>94.6</td>
<td>130.6</td>
</tr>
<tr>
<td></td>
<td>PBESOL</td>
<td>3.171</td>
<td>5.160</td>
<td>378.0</td>
<td>419.4</td>
<td>107.1</td>
<td>144.3</td>
</tr>
<tr>
<td></td>
<td>PBE0</td>
<td>3.178</td>
<td>5.158</td>
<td>396.6</td>
<td>432.3</td>
<td>108.0</td>
<td>146.4</td>
</tr>
<tr>
<td></td>
<td>B3LYP</td>
<td>3.206</td>
<td>5.211</td>
<td>381.3</td>
<td>413.3</td>
<td>91.6</td>
<td>129.3</td>
</tr>
<tr>
<td>Expt.</td>
<td></td>
<td>361.2</td>
<td>390.3</td>
<td>93.1</td>
<td>130.9</td>
<td>98.0</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>PWGGA</td>
<td>3.276</td>
<td>5.278</td>
<td>203.3</td>
<td>215.1</td>
<td>103.3</td>
<td>117.8</td>
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<tr>
<td></td>
<td>PBESOL</td>
<td>3.237</td>
<td>5.220</td>
<td>215.9</td>
<td>229.6</td>
<td>119.2</td>
<td>132.3</td>
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<tr>
<td></td>
<td>PBE0</td>
<td>3.195</td>
<td>5.165</td>
<td>224.9</td>
<td>219.3</td>
<td>112.4</td>
<td>128.5</td>
</tr>
<tr>
<td></td>
<td>HF</td>
<td>0.73</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Expt.</td>
<td></td>
<td>206</td>
<td>211</td>
<td>118</td>
<td>117</td>
<td>44.3</td>
<td></td>
</tr>
<tr>
<td>AlN</td>
<td>PWGGA</td>
<td>3.125</td>
<td>5.008</td>
<td>393.5</td>
<td>377.9</td>
<td>104.6</td>
<td>136.3</td>
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<tr>
<td></td>
<td>PBESOL</td>
<td>3.111</td>
<td>4.980</td>
<td>397.0</td>
<td>376.9</td>
<td>114.2</td>
<td>145.6</td>
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<tr>
<td></td>
<td>PBE0</td>
<td>3.105</td>
<td>4.966</td>
<td>424.0</td>
<td>401.9</td>
<td>115.0</td>
<td>148.6</td>
</tr>
<tr>
<td></td>
<td>B3LYP</td>
<td>3.118</td>
<td>5.003</td>
<td>420.9</td>
<td>407.3</td>
<td>99.3</td>
<td>134.3</td>
</tr>
<tr>
<td></td>
<td>HF</td>
<td>410.5</td>
<td>388.5</td>
<td>98.9</td>
<td>148.5</td>
<td>124.6</td>
<td></td>
</tr>
<tr>
<td>Expt.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For comparison purposes, we present complete results for all three species in Table II, together with previously calculated values and experimental results when available. Nakamura et al. provided experimental results which differ strongly from the other available values reported in Table II. A discussion on this discrepancy is provided by the author in the mentioned paper.

The standard units for piezoelectric constants (per-volume) are C/m$^2$. To convert these to per-atom units of $10^{-16}$ C/Å/atom, the following relationship is used:

$$e_{ik} = e_{ik}(10^{-16} \mu C \times \AA/\text{atom}) N_{\text{atoms}}/V_{\text{cell}}.$$  \hspace{1cm} (28)

V. SURFACE PIEZOELECTRIC PROPERTIES
PARAMETERS CALCULATIONS

For wurtzite, the full matrix of surface piezoelectric constants for GaN, ZnO and AlN nanowire is defined as

$$e^s = \begin{bmatrix} 0 & 0 & e_{15}^s \\ e_{31}^s & e_{33}^s & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$  \hspace{1cm} (29)

We have proposed in our previous papers a methodology to identify surface elastic parameters associated to an infinitely thin surface from atomistic slab models. In this work, we extend this procedure to compute the surface piezoelectric parameters. As the isolated surface does not exist in nature, we have to proceed via a series of slab calculations with (1010) free surfaces, varying the number of atomic layers $n$ in the slab, see Figure 2. The number of atoms in the slab unit cell is $N = 4n$. To avoid the ambiguity of defining slab and surface widths, and assuming that surface corresponds to 1 atomic layer (including atoms of both types), we plot the per-atom properties (energy of polarization) as a function of surface atomic weight $w = 2/n$ where factor 2 comes from free surfaces on both sides of the slab. Assuming additive model, the dependence should be linear, e.g.

$$P_{i}^{\text{slab}}(w) = w P_{i}^{\text{surf}} + (1-w)P_{i}^{\text{slab}}(w \to 0).$$  \hspace{1cm} (30)
leading to a similar relation for slab per-atom piezoelectric coefficient

\[ e_{ij}^{\text{slab}}(w) = w e_{ij}^{\text{surf}} + (1 - w) e_{ij}^{\text{slab}}(w \to 0). \] (31)

The limiting values \( e_{ij}^{\text{slab}}(w \to 0) \) are related to bulk parameters as:

\[ e_{33}^{\text{slab}}(w \to 0) = e_{33}^{\text{bulk}} - \frac{C_{13}^{\text{bulk}}}{C_{33}^{\text{bulk}}} e_{31}^{\text{slab}} \] (32)

\[ e_{31}^{\text{slab}}(w \to 0) = e_{31}^{\text{bulk}} \frac{C_{11}^{\text{bulk}}}{C_{12}^{\text{bulk}}} - \frac{C_{12}^{\text{bulk}}}{C_{11}^{\text{bulk}}} e_{33}^{\text{slab}} \] (33)

and \( e_{15}^{\text{slab}}(w \to 0) = e_{15}^{\text{bulk}} \).

Thus, by fitting \( e_{ij}^{\text{slab}}(w) \) to a linear function, we can obtain the surface per-atom piezoelectric coefficients which can be further converted to per-surface units, to be used in continuous model, via

\[ e_s^{ik} (\text{nC/m}) = \frac{4}{ac} e_s^{ik} (10^{-32} \text{Cm/atom}). \] (34)

using the fact that surface unit cell contains 4 atoms and has an area of \( S = ac \) with a and c being bulk unit cell parameters.

In figures 3, 4 and 5, we show the plots of the \( e_{33}, e_{31} \) and \( e_{15} \) coefficients as a function of \( w \), for GaN, ZnO and AlN materials. We note that the linear model is generally very good with one exception of \( e_{33} \) coefficient for ZnO. For the latter case, the coefficient \( e_{33} \) varies very little with slab size and stays close to bulk value. This, most probably, indicates that surface and bulk parameters are practically identical and the variation is caused by numerical errors.

Finally, the computed values of the surface coefficients, using different DFT functionals, are summarized in Table IV. Note that the values differ significantly from the results obtained by Li et al. and Dai et al. The main reason is the difference between the studied systems. In the mentioned papers the free surfaces considered in the slab model were (0001) surfaces and the sample was stretched in the direction normal to this surface.

Elastic surface properties for ZnO and AlN have been computed in our previous papers. In this work, we also calculated elastic surface constants for GaN. For wurtzite, there are four elastic surface constants \( C_{11}^s, C_{13}^s, C_{33}^s \), and \( C_{55}^s \) and two residual stress components \( \tau_1^s, \tau_3^s \) (see Table III). Conversion from Hartree/atom to N/m is done through \( C(\text{N/m}) = \frac{4}{3} C(\text{Hartree/atom}) \).
FIG. 4: Plots of $e_{31}^{a,\text{slab}}$ (in $10^{-32}$ Cm/atom) as a function of surface weight $w$, used for computing the surface piezoelectric parameter $e_{31}$ for GaN, ZnO and AlN.

The surface parameters obtained in this way from slab calculations, are then used to model the nanowire parameters. Clearly, for small nanowires, the surface structure can be different from slab affecting the wire properties. However, for nanowires of bigger diameters which are the objects of present continuum model, the difference will show up only at nanowire corners, which represent a small portion of total atoms and can be thus safely neglected. The good agreement between ab initio results and continuum model, as described in next sections, is an indirect proof of the validity of such an assumption. Still, the structure of surface and the corners of nanowire may certainly be of interest and we plan to publish a detailed study elsewhere. Briefly, we found that while the outmost surface atoms of metal are diving into the bulk, the corner atoms are more relaxed and less shifted. To give a brief example: for ZnO surface and using PWGGA functional, the Zn atoms go in by about 0.32 Å in slabs (compared to experimental values of 0.45 (LEED), 0.06 (GIXD) and 0.37 (HRTEM)), the central Zn atom on

FIG. 5: Plots of $e_{15}^{a,\text{slab}}$ (in $10^{-32}$ Cm/atom) as a function of surface weight $w$, used for computing the surface piezoelectric parameter $e_{15}$ for GaN, ZnO and AlN.
TABLE III: Surface elastic parameters (in N/m).

<table>
<thead>
<tr>
<th>Method</th>
<th>$C_{11}$</th>
<th>$C_{33}$</th>
<th>$C_{13}$</th>
<th>$C_{22}$</th>
<th>$\tau_1^3$</th>
<th>$\tau_3^3$</th>
</tr>
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<tbody>
<tr>
<td><strong>GaN</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PWGGA</td>
<td>99.0</td>
<td>78.7</td>
<td>18.2</td>
<td>33.8</td>
<td>-1.59</td>
<td>-1.00</td>
</tr>
<tr>
<td>PBESOL</td>
<td>99.6</td>
<td>79.9</td>
<td>18.3</td>
<td>33.8</td>
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<td>-1.07</td>
</tr>
<tr>
<td>PBE0</td>
<td>107.3</td>
<td>86.5</td>
<td>21.4</td>
<td>37.2</td>
<td>-1.97</td>
<td>-1.18</td>
</tr>
<tr>
<td><strong>ZnO</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PWGGA</td>
<td>44.2</td>
<td>35.0</td>
<td>14.2</td>
<td>11.7</td>
<td>-1.80</td>
<td>-1.30</td>
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<tr>
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<td>32.8</td>
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<tr>
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<td><strong>AlN</strong></td>
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</tr>
<tr>
<td>PWGGA</td>
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<td>68.0</td>
<td>21.2</td>
<td>39.9</td>
<td>-2.20</td>
<td>-0.78</td>
</tr>
<tr>
<td>PBESOL</td>
<td>99.2</td>
<td>64.6</td>
<td>21.0</td>
<td>39.2</td>
<td>-2.33</td>
<td>-0.71</td>
</tr>
<tr>
<td>PBE0</td>
<td>109.6</td>
<td>72.7</td>
<td>23.0</td>
<td>43.4</td>
<td>-2.49</td>
<td>-0.87</td>
</tr>
<tr>
<td>B3LYP</td>
<td>114.1</td>
<td>78.0</td>
<td>22.3</td>
<td>44.3</td>
<td>-2.33</td>
<td>-0.87</td>
</tr>
</tbody>
</table>
TABLE V: Effective first-principles piezoelectric parameter $e_{33}^{eff}$ (in $C/m^2$) of GaN nanowire for different diameters $d$ (in nm). Bulk value from\textsuperscript{10} is a bulk parameter which is somewhat smaller than limiting $e_{33}^{eff}$ value that also includes contribution from bulk $e_{33}$.

<table>
<thead>
<tr>
<th>$n$</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>$\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>48</td>
<td>108</td>
<td>192</td>
<td>300</td>
<td>432</td>
<td>588</td>
<td></td>
</tr>
</tbody>
</table>

**PBESOL**

<table>
<thead>
<tr>
<th>$d$</th>
<th>0.634</th>
<th>1.268</th>
<th>1.902</th>
<th>2.536</th>
<th>3.171</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_{33}^{eff}$</td>
<td>5.909</td>
<td>3.067</td>
<td>1.971</td>
<td>1.778</td>
<td>1.125</td>
</tr>
</tbody>
</table>

**PBE0**

<table>
<thead>
<tr>
<th>$d$</th>
<th>0.636</th>
<th>1.271</th>
<th>1.907</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_{33}^{eff}$</td>
<td>6.003</td>
<td>3.127</td>
<td>2.358</td>
</tr>
</tbody>
</table>

**PWGGA**

<table>
<thead>
<tr>
<th>$d$</th>
<th>0.64</th>
<th>1.280</th>
<th>1.920</th>
<th>2.560</th>
<th>3.200</th>
<th>3.840</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_{33}^{eff}$</td>
<td>5.299</td>
<td>2.699</td>
<td>2.025</td>
<td>1.715</td>
<td>1.541</td>
<td>1.428</td>
</tr>
</tbody>
</table>

Reference.\textsuperscript{10}

$e_{33}$ | 7.6 | 0.554 |

FIG. 6: Effective piezoelectric coefficients $e_{33}^{eff}$ of GaN nanowire as a function of the diameter; comparison between continuum FEM model and first-principles calculations using PBESOL, PBE0, PWGGA functionals.

TABLE VI: Effective first-principles piezoelectric parameter $e_{33}^{eff}$ (in $C/m^2$) of ZnO nanowire, with different diameters $d$ (in nm). See also caption of Table.V

<table>
<thead>
<tr>
<th>$n$</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>$\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>48</td>
<td>108</td>
<td>192</td>
<td>300</td>
<td>432</td>
<td>588</td>
<td></td>
</tr>
</tbody>
</table>

**PBESOL**

<table>
<thead>
<tr>
<th>$d$</th>
<th>0.647</th>
<th>1.295</th>
<th>1.942</th>
<th>2.589</th>
<th>3.237</th>
<th>3.884</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_{33}^{eff}$</td>
<td>7.995</td>
<td>4.376</td>
<td>3.422</td>
<td>2.992</td>
<td>2.749</td>
<td>2.593</td>
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</tbody>
</table>

**PWGGA**

<table>
<thead>
<tr>
<th>$d$</th>
<th>0.656</th>
<th>1.311</th>
<th>1.966</th>
<th>2.622</th>
<th>3.277</th>
<th>3.933</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_{33}^{eff}$</td>
<td>7.324</td>
<td>3.956</td>
<td>3.125</td>
<td>2.817</td>
<td>2.495</td>
<td>2.357</td>
</tr>
</tbody>
</table>

Reference.\textsuperscript{21}

$e_{33}$ | 6.52 | 3.75 | 3.13 | 2.72 | 1.29 |

Reference.\textsuperscript{10}

$e_{33}$ | 18.1 | 1.18 |

FIG. 7: Effective piezoelectric coefficients $e_{33}^{eff}$ of ZnO nanowire as a function of the diameter; comparison between continuum FEM model and first-principles calculations using PBESOL, PBE0, PWGGA functionals.

TABLE VII: Effective first-principles piezoelectric parameter $e_{33}^{eff}$ (in $C/m^2$) of AlN nanowire, with different diameters $d$ (in nm).

<table>
<thead>
<tr>
<th>$n$</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>$\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>48</td>
<td>108</td>
<td>192</td>
<td>300</td>
<td>432</td>
<td>588</td>
<td></td>
</tr>
</tbody>
</table>

**PBESOL**

<table>
<thead>
<tr>
<th>$d$</th>
<th>0.622</th>
<th>1.247</th>
<th>1.867</th>
<th>2.489</th>
<th>3.115</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_{33}^{eff}$</td>
<td>9.402</td>
<td>5.048</td>
<td>3.870</td>
<td>3.337</td>
<td>3.032</td>
</tr>
</tbody>
</table>

**PBE0**

<table>
<thead>
<tr>
<th>$d$</th>
<th>0.621</th>
<th>1.242</th>
<th>1.863</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_{33}^{eff}$</td>
<td>9.145</td>
<td>4.873</td>
<td>3.733</td>
</tr>
</tbody>
</table>

**PWGGA**

<table>
<thead>
<tr>
<th>$d$</th>
<th>0.624</th>
<th>1.249</th>
<th>1.873</th>
<th>2.497</th>
<th>3.121</th>
<th>3.746</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_{33}^{eff}$</td>
<td>8.687</td>
<td>4.620</td>
<td>3.534</td>
<td>3.029</td>
<td>2.753</td>
<td>2.571</td>
</tr>
</tbody>
</table>

$e_{33}$ | 8.18 |

Plots of the results comparing the values of the effective piezoelectric coefficients $e_{33}^{eff}$ obtained by the full first-principles and the continuum model are presented in figures 6, 7 and 8 for GaN, ZnO and AlN, respectively. For each DFT calculation, PWGGA, PBESOL and PBE0 functionals have been used. We can notice a very good agreement between continuous and first-principles results for all materials.

The continuum model allows for computing the non-uniform strain, stress and polarization fields in the nanowire submitted to an arbitrary load, and for arbitrary sizes of nanowires. In figure 9, we show the polarization field and the distorted surface of a GaN nanowire in absence of load and without electrical field for diam-
VII. CONCLUSIONS

We have proposed a methodology for computation of the surface piezoelectric coefficients for (110) surfaces and provide the numerical values for wurtzite AlN, GaN and ZnO nanowires. The coefficients can be used within a continuum piezoelectric model extended with a surface energy. We have solved the equations of the continuum model with a finite element technique and compared the results with full first-principles calculations of nanowires with diameters ranging from 0.6 nm to 3.9 nm. A good agreement is found between the continuum and first-principles results for the effective piezoelectric coefficient along the axial direction of the nanowire. For all materials, an increase of the effective piezoelectric coefficients is found when the diameter of the nanowire decreases.

FIG. 8: Effective piezoelectric coefficients $e_{33}^{eff}$ of AlN nanowire as a function of the diameter; comparison between continuum FEM model and first-principles calculations using PBESOL, PBE, PWGGA functionals.

**References**

1. Electronic address: julien.yvonnet@univ-paris-est.fr
31. A. Mitrushchenkov, G. Chambaud, J. Yvonnet and Q.-C. He, Nanotech. 21, 255702 (2010).
FIG. 9: Magnified strains and $P_3 \times 10^{-21} \text{C/m}^2$ polarization field in GaN nanowire under free relaxation with the continuum FEM model and different diameters: (a) $d=1$ nm; (b) $d=3$ nm; (c) $d=100$ nm. We can note the size effects with the variation of the diameter.