NANO LETTERS

LETTER

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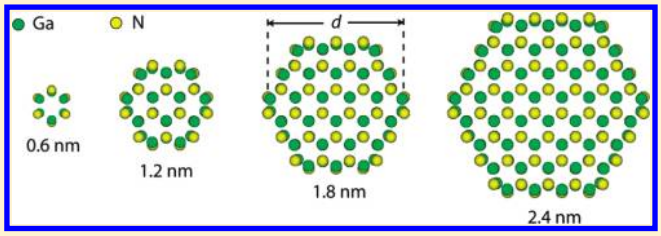
Giant Piezoelectric Size Effects in Zinc Oxide and Gallium Nitride Nanowires. A First Principles Investigation

Ravi Agrawal and Horacio D. Espinosa*

Department of Mechanical Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3111, United States

ABSTRACT: Nanowires made of materials with noncentrosymmetric crystal structure are under investigation for their piezoelectric properties and suitability as building blocks for next-generation self-powered nanodevices. In this work, we investigate the size dependence of piezoelectric coefficients in nanowires of two such materials − zinc oxide and gallium nitride. Nanowires, oriented along their polar axis, ranging from 0.6 to 2.4 nm in diameter were modeled quantum mechanically. A giant piezoelectric size effect is identified for both GaN and ZnO nanowires. However, GaN exhibits a larger and more extended size dependence than ZnO. The observed size effect is discussed in the context of charge redistribution near the free surfaces leading to changes in local polarization. The study reveals that local changes in polarization and reduction of unit cell volume with respect to bulk values lead to the observed size effect. These results have strong implication in the field of energy harvesting, as piezoelectric voltage output scales with the piezoelectric coefficient.



KEYWORDS: Gallium nitride, zinc oxide, nanowires, density functional theory, piezoelectric properties

Piezoelectricity is a phenomenon in which an electric field is generated inside a material subjected to a mechanical strain or vice versa. It is caused by the nonsymmetric crystal structure of certain materials, which results in an effective change in polarization in response to an applied mechanical strain. The strained material behaves like a charged capacitor with an electrostatic potential across it, which can be utilized in sensing, actuation, and energy harvesting applications. Therefore, piezoelectricity provides a direct means of conversion between mechanical and electrical energy. However, at the macroscale, the electrical energy output is relatively low in comparison to mechanical energy required to strain the material. Thus at large scales, applications of piezoelectric devices are typically limited to sensors (e.g., pressure sensors[1]) and actuators (e.g., in atomic force microscopy[2]) where efficiency is not critical. By contrast, nanoscale offers an advantage, that is, the forces required to deform nanostructures made of piezoelectric materials are small enough to be extracted from natural sources of mechanical energy (e.g., ambient noise, wind energy, body movements, and flowing water). Therefore, thin films and nanowires are considered suitable building blocks for next-generation energy-harvesting devices.[3,4] In addition, as the size of these structures is reduced to the nanoscale (thin films and nanowires (NWs)), the conversion efficiency can be improved dramatically for the following reasons: (i) nanomaterials tolerate relatively large deformations prior to failure, which is critical as the electrostatic potential generated (V) is proportional to the applied strain (ε) and piezoelectric coefficient (d_{33}), namely $V \propto d_{33}\varepsilon$; (ii) material properties are often enhanced at the nanoscale relative to the bulk due to surface effects and high surface-to-volume ratios.

Recently, Wang et al. showed that ZnO NWs can act as piezoelectric nanogenerators both by deflecting individual NWs[5] and by integrating them in hybrid microfiber assemblies.[6] NW nanogenerators were also used to convert biomechanical energy (movement of a human finger and body motion of a hamster) to electrical energy.[7]

Various experimental studies have probed either the electrical[8−10] or mechanical[11−16] behavior of nanowires separately; however, electromechanical coupling and its potential size-effects have not been adequately addressed. The challenges associated with such experiments include (i) difficulties in sample manipulation at the nanoscale, (ii) making appropriate electrical measurements accounting for contact resistances, (iii) measuring currents and voltages with sufficiently high resolution, and so forth. The difficulties in conducting such experiments seem to be the primary reason for a large scatter observed in the experimentally reported piezoelectric coefficients for ZnO nanostructures. For example, piezoresponse force microscopy (PFM) has revealed piezoelectric coefficient ranging from 4.41 to 7.5 pm/V for ZnO nanorods with diameters in the 150−500 nm range,[17,18] as well as values ranging from 14.3 to 26.7 pm/V for ZnO nanobelts tens of nm in thickness.[19] On the contrary, a resonance shift method has revealed a value as high as 12 000 pm/V for a 230 nm ZnO nanowire,[20] as compared to a bulk value of 12.4 pm/V.[21,22]

In this work, we investigate piezoelectric size effects from a computational standpoint. First principles-based density functional theory (DFT) calculations were performed to model

Received: November 15, 2010
Revised: December 19, 2010
Published: January 11, 2011

nanowires of zinc oxide and gallium nitride with hexagonal cross sections and with diameters ranging from 0.6 to 2.4 nm. Size dependent trends for piezoelectric coefficients were identified and an analysis of distribution of charges and dipole moments was performed in order to understand the observed size dependence.

The SIESTA[23] software was used for conducting the DFT calculations. The generalized gradient approximation (GGA) using the Perdew−Burke−Ernzerhof (PBE) functional and the revised PBE functional with double-ζ polarization (DZP) orbital basis sets was used. Pseudopotentials for all the atomic species were generated using the Troullier−Martins scheme,[24] and are available via the SIESTA homepage.[25] As d-orbitals play an important role in bonding in case of transition metals, the effect of d-orbital cutoff radius was also investigated for the case of GaN. A smaller cutoff radius (than the cutoff radius available with SIESTA pseudopotentials) was used following the work of Carter et al.[26−28] The cutoff radii used for generating two sets of pseudopotentials for GaN are shown in Table 1. For both ZnO and GaN, 3d-orbital electrons were modeled as the valence electrons to allow for their interaction in bond formation as should be the case with transition metal elements.

To keep the computational costs low, the model sizes were limited to one lattice constant along the polar axis of the nanowire with periodic boundary conditions applied. The convergence of density of k-space mesh-points was studied and Monkhorst pack grid of 1 × 1 × 5 was used for these calculations.[29] To validate the modeling approach and pseudopotentials employed, bulk piezoelectric coefficients were first calculated for both GaN and ZnO. Table 2 shows the bulk properties as calculated for ZnO and GaN. A comparison between our calculations and values reported in the literature is also provided. The piezoelectric coefficient for bulk GaN, as calculated using PSP1, was found to be smaller than the value reported for bulk. As we were interested in the size dependent trends, calculations were pursued with both pseudopotentials for GaN to investigate how the definition of the d-orbital affects the results.

Nanowire cross sections as a function of wire diameter are shown in Figure 1 together with the relaxed atomic positions. To calculate the piezoelectric coefficients (d_{33}), the nanowires were strained along the polar axis at fixed increments of 0.5% strain up to 4% strain. The energy of the strained configurations was first minimized and then their polarization was calculated using the Berry-phase approach.[33] The polarization per unit volume was plotted as a function of strain, the slope of which yielded the piezoelectric coefficient for a given nanowire material and size.[34]

Figure 2a shows the piezoelectric coefficients for ZnO and GaN nanowires, as a function of their diameter, calculated using the PBE functional. In Figure 2b, the values are normalized with respect to the bulk piezoelectric coefficients to reveal the size dependent enhancement. These results suggest that, for both ZnO and GaN nanowires, approximately 2 orders of magnitude improvement in piezoelectric coefficients can be attained if the nanowire diameter is reduced to less than 1 nm. The results also show that for GaN the strong piezoelectric enhancement extends to diameters well in excess of 2.5 nm. By contrast, the enhancement is much attenuated for ZnO nanowires with diameters larger than 1.5 nm.

The investigation reveals that the computed piezoelectric coefficients are highly dependent on the chosen pseudopotentials and functionals. Table 3 compares the predictions of PBE and RPBE functionals for NWs made of the two materials. The RPBE functional revealed smaller piezoelectric coefficient as compared to PBE functional in the case of ZnO; however, the differences in PBE/RPBE predictions were small for GaN. These differences suggest that further insight from experiments is necessary to validate the use of one functional over another for modeling electromechanical properties in nanowires.

In Table 4, the results obtained for GaN nanowires using two different pseudopotentials for Ga-atoms are compared. PSP1 with higher cutoff radius for the 3d-orbital, predicts higher piezoelectric coefficients as compared to PSP2. It is noteworthy that the PSP1 underestimates the bulk value as compared to PSP2. This means that PSP1 predicts stronger size dependence as compared to PSP2.

To further understand the origin of this size dependence, the effect of atomic restructuring was decoupled from the change in absolute value of polarization. Figure 3a shows the polarization

Table 1. Difference in Cut-off Radii of the Two Sets of Pseudopotentials (PSP) Used for Ga and N Atoms

atom type	Cut-off radii for s, p, d, and f orbitals (Å)	
	PSP1	PSP2
Ga	2.18, 2.35, 2.18, 2.59	2.0, 2.0, 1.2, 2.38
N	1.48, 1.48, 1.48, 1.48	1.5, 1.5, 1.5, 1.5

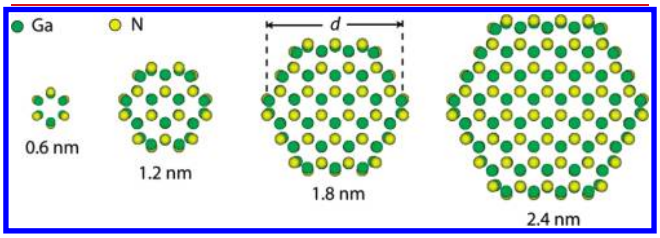


Figure 1. Cross sections of modeled GaN nanowires after energy minimization.

Table 2. Bulk Properties of ZnO and GaN[a]

material property	literature		our calculations		
	ZnO	GaN	ZnO	GaN (PSP1)	GaN (PSP2)
lattice constant a (Å)	3.26,[30] 3.286[31]	3.198,[32] 3.28[28]	3.25	3.283	3.281
c/a	1.616,[30] 1.595[31]	1.634,[32] 1.619[28]	1.634	1.628	1.617
c_{33}(GPa)		354[32]		344	323
e_{33} (C/m^2)	1.19[31]	0.66[32]	1.18	0.255	0.554

[a] For GaN, values obtained using two different PSPs are reported.

dx.doi.org/10.1021/nl104004d |Nano Lett. 2011, 11, 786–790

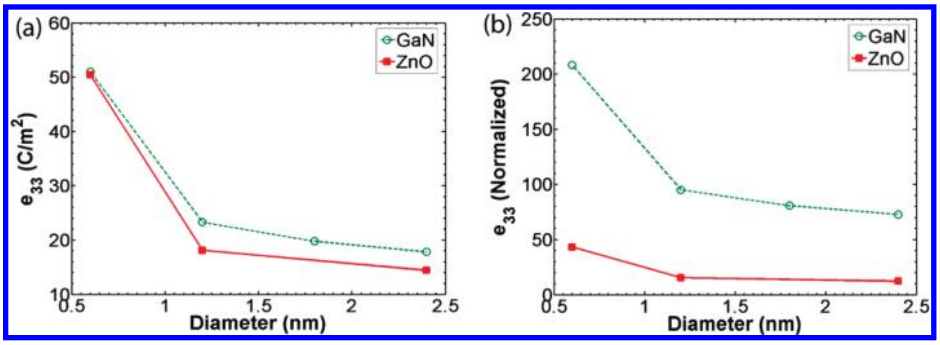


Figure 2. Piezoelectric coefficients of GaN and ZnO nanowires as a function of their diameter. (a) Absolute values; (b) normalized with respect to the respective bulk values. Values reported in these figures used PBE and RPBE functionals for GaN and ZnO, respectively. For GaN, results from PSP1 are reported.

Table 3. Differences in Piezoelectric Coefficient Computed Using PBE and RPBE Functional

diameter (nm)	ZnO (C/m^2)		GaN (PSP1, C/m^2)	
	PBE	RPBE	PBE	RPBE
0.6	97.1	50.4	51.0	58.8
1.2	35.5	18.1	23.3	19.9

Table 4. Effect of 3d-Orbital Radius Chosen for Modeling Ga Atoms in GaN Nanowires

diameter (nm)	GaN (C/m^2)	
	PSP1	PSP2
0.6	51.0	25.8
1.2	23.3	7.6
bulk	0.255	0.554

(per atom) as a function of strain for GaN nanowires of different diameter using PSP1 and the PBE functional. It is noteworthy that the absolute value of polarization for nanowires is smaller than that of bulk. On the contrary, when the polarization per unit volume is plotted (shown in Figure 3b), the trend is reversed. This asserts that the reduction in volume of nanowires due to restructuring of the surface atoms (surface reconstruction) plays a significant role in enhancing the piezoelectric properties of the nanowires. Note that the volume for each nanowire was computed from the diameter (d, as shown in Figure 1) using the formula $V = (3\sqrt{3}/8)d^2L$, with L being the length of the unit cell.

Furthermore, to understand why the overall polarization per atom for nanowires is smaller than that of bulk, Mulliken charges were used to calculate the first-order dipole moment of atomic pairs of Ga and N atoms. At each radial location, local dipole moment of each pair of atoms was calculated using the following summation

$$\mu_{\text{dipole}} = \sum q d_{ij} \tag{8}$$

where q is the average charge on each atomic pair and d_{ij} is the interatomic distance between them along the axial direction. This first-order dipole moment is plotted as a function of atomic radial coordinate in Figure 4b−d for two GaN nanowires of different diameters. Figure 4a shows the radial coordinate, r, for a set of atoms lying on the dotted circle for a 1.8 nm nanowire. The dipole moment per atomic pair, as measured for bulk GaN, is also plotted for reference as a dashed line in Figure 4.

The reduced dipole moment with respect to bulk, as observed for nanowires, is in general agreement with the reduced polarization for nanowires as shown in Figure 3. However, the volume of nanowires is smaller as compared to the bulk value (as shown in Figure 5a). This plays an important role in enhancing the piezoelectric coefficient, which depends on the polarization per unit volume. The charge redistribution in GaN nanowires was also analyzed and is shown in Figure 5b, which reveals that charge deviates from bulk behavior primarily on the surface of the nanowires. These findings assert that interatomic rearrangement also plays an important role in affecting polarization. The overall charge redistribution and interatomic rearrangement in the axial direction of nanowires has the net effect to reduce polarization. However, the contraction in the radial direction, due to surface relaxation, leads to a reduction in overall nanowire volume with respect to a bulk crystal with the same number of atoms. This reduction in volume, in essence, causes the observed enhancement in piezoelectric coefficients.

In summary, quantum mechanical computational estimates of piezoelectric coefficients in nanowires were reported. The investigation revealed giant piezoelectric coefficients in both GaN and ZnO nanowires as a result of size effects. For GaN, diameters well in excess of 2.5 nm are required to converge to bulk values. These results demonstrate that the full potential of nanowire systems in actuation, sensing and energy harvesting applications is far from being fully exploited. Particularly, in the field of energy harvesting to develop self-powered devices,[35] piezoelectric output voltage, which is proportional to piezoelectric coefficient,[36] can be improved by 1−2 orders of magnitude by reducing the size of nanowires used in the design of such systems. The findings reported here, therefore, suggest new research directions. In particular, the need for experimental confirmation of the theoretical predictions is highly needed to gain further insight into the phenomenon. Clearly, measurement of piezoelectric coefficients in nanowires with diameters below 20 nm is very challenging and a topic of high interest within the nanotechnology community. In this regard, this work also provides direction for the development of new computational tools, for example, based on classical molecular dynamics,[37] which can be used to model larger nanowires that cannot be investigated using DFT.

On the basis of the charge distribution analysis and calculation of first-order dipole moments, overall polarization is found to be reduced in nanowires as compared to bulk. However, the piezoelectric coefficients are found to be much higher due to surface relaxation induced volume reductions in nanowires. The study

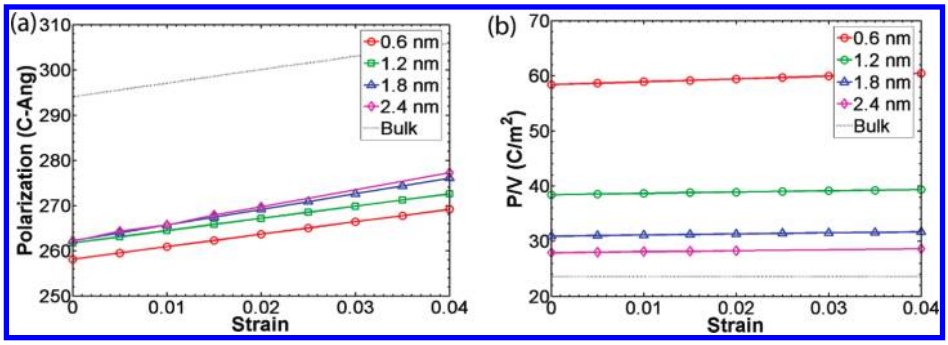


Figure 3. (a) Polarization (per atom) as a function of strain for GaN nanowires of different diameters; (b) polarization per unit volume for different nanowires.

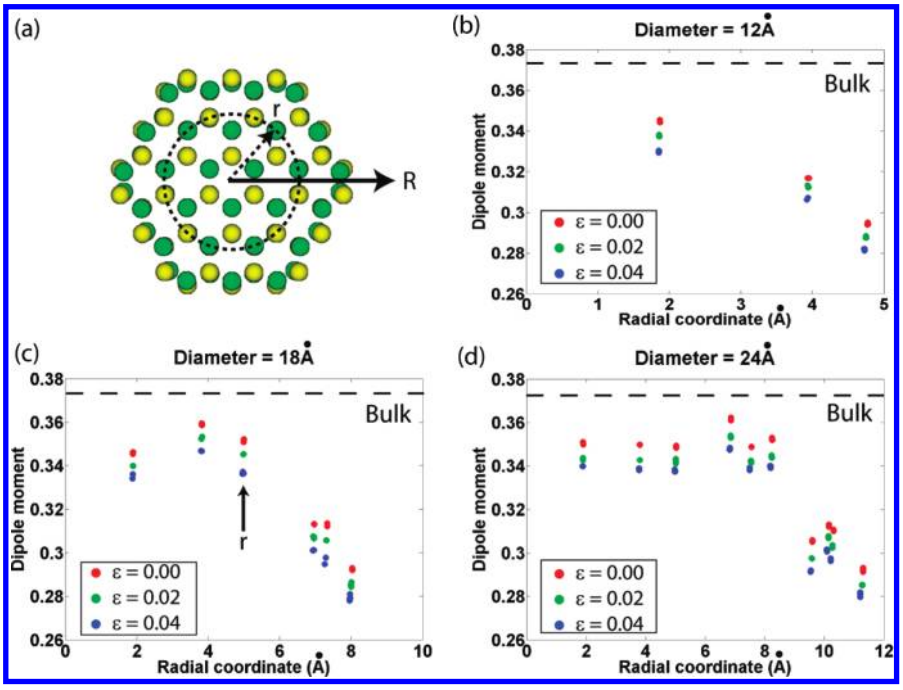


Figure 4. (a) Schematic showing the radial coordinate, *r*, for a set of atoms lying on the dotted circle. (b−d) First-order dipole moment calculated based on interatomic distances and Mulliken charges for nanowires of different diameter. Units of dipole moment are eÅ, where e is the electronic charge. Note that no atoms lie on $r = 0$.

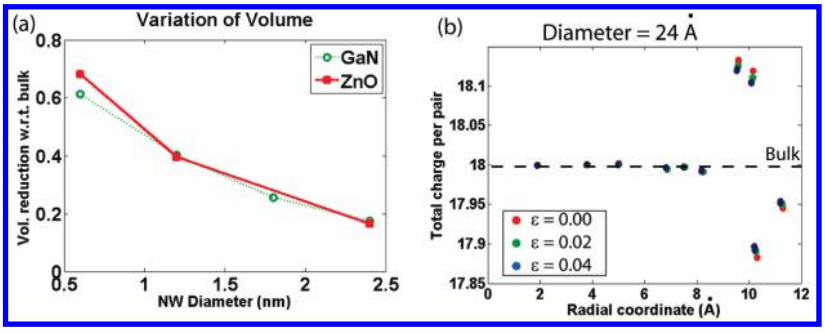


Figure 5. (a) Reduction in volume of NW per Ga−N pair with respect to bulk volume for GaN and ZnO NWs; (b) charge distribution per Ga−N pair as a function of radial coordinate for 2.4 nm diameter GaN nanowire at different strains. Dotted line represents the bulk value of 18 for each Ga−N pair.

also uncovered the fact that the absolute values of piezoelectric coefficients appear to be strongly influenced by the functionals and/or pseudopotentials being employed. More insight from experimentation is highly desirable to validate the applicability of the approximations used in the reported quantum mechanical computations.

AUTHOR INFORMATION

Corresponding Author
*Phone: (847) 467-5989. Fax: (847) 491-3915. E-mail: espinosa@northwestern.edu.

ACKNOWLEDGMENT

H.D.E. acknowledges the support from the National Science Foundation through Award Numbers DMR-0907196 and CMMI-0555734. We are thankful to Dr. Jeffrey T. Paci for insightful discussions. A special thanks is due to George Schatz and Susan Trolier McKinstry for reading and commenting on the manuscript. This work was also supported in part by the National Science Foundation through TeraGrid resources provided by Indiana University. In particular, the authors would like to thank Ray Sheppard at Indiana University for hardware/software support.

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