

Piezoelectricity in ZnO nanowires: A first-principles study

H. J. Xiang, Jinlong Yang,^{a)} J. G. Hou, and Qingshi Zhu

Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

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Hexagonal [0001] nonpassivated ZnO nanowires with diameters up to 2.8 nm are studied with density functional calculations. The authors find that ZnO nanowires have larger effective piezoelectric constant than bulk ZnO due to their free boundary. For ZnO nanowires with diameters larger than 2.8 nm, the effective piezoelectric constant is almost a constant. Surprisingly, the effective piezoelectric constant in small ZnO nanowires does not depend monotonically on the radius due to two competitive effects. Moreover, the quantum confinement effect results in larger band gaps of bare ZnO nanowires compared to that of bulk ZnO. © 2006 American Institute of Physics. [DOI: 10.1063/1.2397013]

ZnO (Ref. 1) is one of the most important materials due to its three key advantages: semiconducting with a direct wide band gap of 3.37 eV and a large excitation binding energy (60 meV), biocompatible and piezoelectric. ZnO nanostructures could have some applications due to their unique physical and chemical properties arising from surface and quantum confinement. Experimentally, piezoelectric properties of ZnO nanostructures have been extensively explored. For example, Gao *et al.* reported the growth of piezoelectric ZnO nanohelix.² Very recently, piezoelectric nanogenerators based on ZnO nanowire arrays have been demonstrated by Wang and Song.³ The effective piezoelectric coefficient of individual (0001) surface dominated ZnO nanobelts measured by piezoresponse force microscopy was found to be much larger than the value for bulk wurtzite ZnO.⁴ In contrast, Fan *et al.* showed that the piezoelectric coefficient for ZnO nanopillar with a diameter about 300 nm is smaller than the bulk values.⁵ On the theoretical side, researches on the piezoelectric properties of ZnO nanowires are still very lacking since the large supercells for simulating ZnO nanowires pose a great challenge for sophisticated calculations.

In this letter, by employing reliable first-principles methods, we have studied the piezoelectric properties of [0001] ZnO nanowires. The effective piezoelectric constant in ZnO nanowires is larger than that of bulk ZnO due to the free boundary of nanowires. For ZnO nanowires with a diameter larger than 2.8 nm, the effective piezoelectric constant is almost a constant. Moreover, the effective piezoelectric constant in small ZnO nanowires does not depend monotonically on the radius due to two competitive effects. In addition, the band gap increases along with the decrease of the radius of ZnO nanowires due to the radial confinement.

Our calculations are performed using the SIESTA package.⁶ The local density approximation⁷ (LDA) to the exchange correlation functional is employed. The double- ζ polarized numerical atomic orbitals basis sets for both Zn and O with an energy shift parameter of 20 mRy are used. Bulk ZnO has a wurtzite structure with a noncentrosymmetric symmetry, resulting in a perpendicular dipole moment

and spontaneous polarization along the c axis. The computed (experimental⁸) lattice parameters of bulk wurtzite ZnO are $a=3.17$ Å (3.25 Å), $c=5.18$ (5.20 Å), $u=0.374$ (0.381). The calculated LDA direct band gap is 0.63 eV, in good agreement with other LDA results.^{9,10}

Here we mainly focus on bare [0001] ZnO nanowires since almost all ZnO nanowires grow along the [0001] direction with six facet $\{10\bar{1}0\}$ surfaces with low surface energy.^{11,12} The nanowires are modeled by hexagonal supercells whose lateral lattice constants are so large that there is almost no interaction between the nanowires. Five ZnO nanowires (shown in Fig. 1) with diameters ranging from about 0.3 to 2.8 nm, labeled as A, B, C, D, and E, are examined. The largest nanowire, E, contains 300 atoms in the unit cell.

Before we proceed to study the piezoelectric properties of ZnO nanowires, we first discuss their structural and electronic properties. Since the lattice constant of small ZnO nanowires might differ significantly from the bulk counterpart, we optimize both the lattice constant c and internal coordinates of nanowires. The relaxed structures of these ZnO nanowires are shown in Fig. 1. Since both surface Zn and O atoms move inwards and Zn atoms move much more,

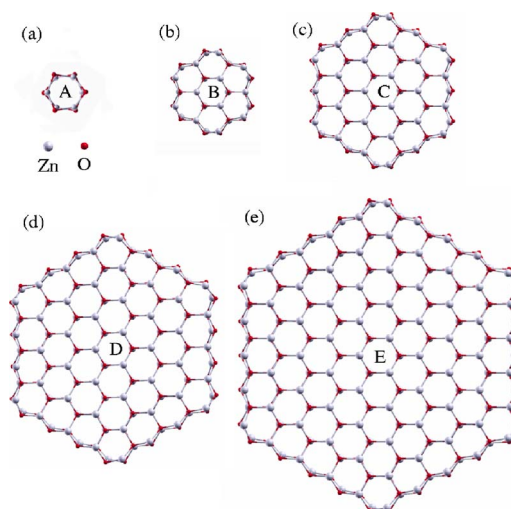


FIG. 1. Relaxed structures for ZnO nanowires with different radii. We label these nanowires as A, B, C, D, and E.

^{a)} Author to whom correspondence should be addressed; electronic mail: jlyang@ustc.edu.cn

TABLE I. Unrelaxed diameter (D_0), relaxed diameter (D), relaxed lattice constant (c), band gap (E_g), and effective piezoelectric constant (e_{33}^a) of five different ZnO nanowires (A, B, C, D, and E) and bulk ZnO.

	A	B	C	D	E	Bulk
D_0 (Å)	3.66	9.68	15.96	22.27	28.59	
D (Å)	3.32	9.32	15.61	21.97	28.33	
c (Å)	5.335	5.302	5.270	5.234	5.215	5.180
E_g (eV)	2.40	1.54	1.09	0.85	0.75	0.63
e_{33}^a (10^{-16} $\mu\text{C Å/ion}$)	2025	1837	1879	1986	1961	1453

it looks like surface O atoms rotate outwards. The diameters of relaxed and unrelaxed nanowires are shown in Table I. We can see that the diameters of relaxed nanowires are smaller than those of unrelaxed nanowires by almost 0.3 Å. The relaxation of surface atoms in ZnO nanowires is similar to that in ZnO $[10\bar{1}0]$ surface.¹³ Along with the shrinkage of surface atoms, the lattice constant c of ZnO nanowires is increased when compared with that of bulk ZnO, as shown in Table I. We can see that the elongation of small nanowires is considerably large; however, the lattice constants of large nanowires tend to approach that of bulk ZnO.

Our calculations show that all $[0001]$ ZnO nanowires are semiconducting with a direct band gap at Γ . Although the LDA usually underestimates the band gap, the trend of the band gaps of ZnO nanowires predicted from the LDA calculations are expected to be correct. The LDA band gaps are shown in Table I. Clearly, the band gaps of ZnO nanowires increase monotonically along with the decrease of the radius of nanowires. In comparison with bulk ZnO, the increment of the band gap of nanowire A can be as large as 1.77 eV. The blueshift of the band gap should be due to the quantum confinement effect. However, the gap-widening effect in nonpassivated nanowires is unusual. For example, due to the presence of surface states, nonpassivated Si nanowires grown along the $\langle 100 \rangle$ direction are metallic and semimetallic,¹⁴ and the band gap of AlN nanowires is smaller than that of bulk AlN.¹⁵

To gain an insight into the gap-widening effect in ZnO nanowires, we first briefly discuss the electronic structure of the ZnO $[10\bar{1}0]$ surface.¹³ The valence and conduction bands near the Fermi level are primarily of Zn–O bond-orbital (mainly O $2p$ states) and antibond-orbital (mainly Zn $4s$ states) character, respectively. And there is an O $2p$ -like dangling bonds derived surface state (i.e., P_1) in the top of the valence bands. In ZnO nanowires, there is a radial confinement. Due to the character of the conduction band, it will have a delocalized distribution in the x - y plane and a large dispersion along z . Furthermore, the energy of the conduction band will increase substantially in small radius nanowires due to the radial confinement. On the other hand, the P_1 surface state can be easily confined in the x - y plane and has weak dispersion along z . To verify our argument, in Fig. 2 we plot the band structure and charge density of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) states at Γ of nanowire B. As expected, the LUMO is delocalized in the whole nanowire, and the HOMO is mainly composed of surface O $2p$ -like dangling bonds with an energy only 80 meV above the top of the valence band of bulk ZnO. It is the different response to the radial confinement between the LUMO and

HOMO that leads to the overall gap-widening effect in ZnO nanowires.

Now we turn to the piezoelectric effect in ZnO nanowires. First, the piezoelectric constant e_{33} of bulk ZnO is computed to validate our results. The piezoelectric constants e_{ij} is defined as follows: $e_{ij} = d\mathbf{P}_i/d\epsilon_j$, where \mathbf{P} is the total polarization and ϵ_j is the strain tensor component. Here, the piezoelectric constants are computed by combining the Berry phase method in the modern theory of polarization¹⁶ with the finite difference method. For each structure with a certain degree of strain, the atomic internal coordinates are fully relaxed. The calculated piezoelectric constant e_{33} for bulk ZnO is 1.29 C/m², which accords excellently with other authors' result (1.28 C/m²).⁹

As the conventional definition of piezoelectric constant for three-dimensional bulk is not appropriate for describing the piezoelectric properties of one-dimensional systems, we define the atomic averaged effective piezoelectric constant as $e_{33}^a = e_{33} V_{\text{scell}}/N$, where N is the number of atoms and V_{scell} is the volume of the supercell. The results are presented in Fig. 3(a) and Table I. We can clearly see that e_{33}^a of nanowires is considerably larger than that of bulk ZnO. We find that larger e_{33}^a in nanowires is caused by the free boundary of nanowires. In the calculations of e_{33}^a , the lateral lattice constants are fixed. When bulk ZnO is strained along the c axis, atoms cannot relax freely along the lateral directions. However, when nanowires are compressed or elongated along the c axis, atoms can relax freely along the lateral directions due to the free boundary. Hence, the effective piezoelectric constant e_{33}^a in nanowires should approach $e_{33}^b - 2e_{31}^b \times \nu$, where e_{33}^b and e_{31}^b are effective piezoelectric constants of bulk ZnO and

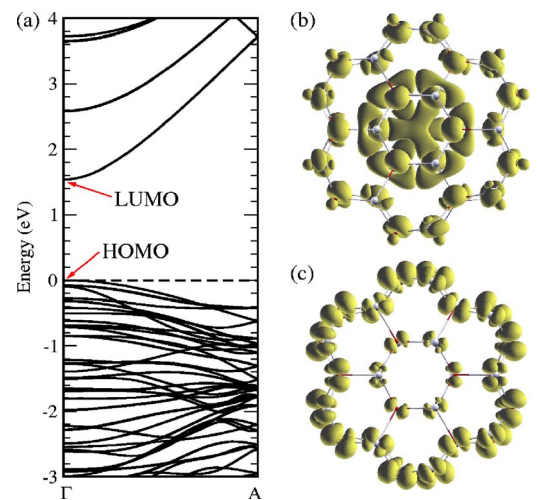


FIG. 2. (a) Band structure of nanowire B. (b) The charge density of the LUMO state at Γ for nanowire B. (c) The charge density of the HOMO state at Γ for nanowire B.

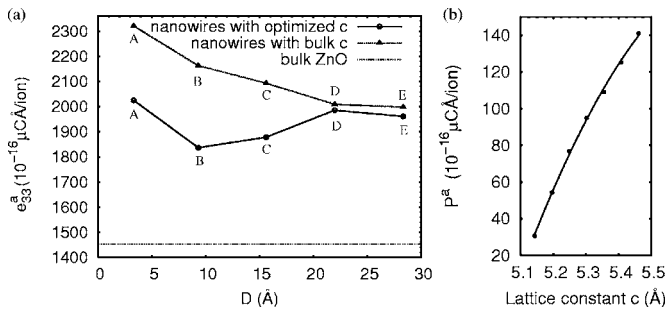


FIG. 3. (a) Dependence of the effective piezoelectric constant e_{33}^a on the diameters of the nanowires with optimized lattice constant c and nanowires with bulk lattice constant c . The horizontal dotted line indicates the piezoelectric constant of bulk ZnO. (b) shows the polarization of ZnO nanowire B with different c .

$\nu = -\epsilon_1/\epsilon_3 = -\epsilon_2/\epsilon_3$ is Poisson's ratio [$\epsilon_1 = \epsilon_2 = (a - a_0)/a_0$, $\epsilon_3 = (c - c_0)/c_0$, a is the relaxed lateral lattice constant when the lattice constant of ZnO is changed to c]. Since $\nu > 0$ and $e_{31}^b < 0$,⁹ e_{33}^a in nanowires is larger than e_{33}^b . For the same reason, the effective piezoelectric coefficient in ZnO nanobelts was also found experimentally to be larger than that of bulk ZnO by Zhao *et al.*⁴ Fan *et al.* suggested that the reduced electromechanical response in ZnO nanopillars might be due to structural defects.⁵ One might expect smaller nanowires to have larger piezoelectric constants due to their larger ratio of surface atoms. However, Fig. 3(a) shows that e_{33}^a does not monotonically depend on the radius of ZnO nanowires: e_{33}^a for nanowire D is larger than that for nanowires C and E. We attribute this abnormal behavior to the increase of the lattice constant along with the decrease of the radius of ZnO nanowires, since the piezoelectric constant of a certain nanowire decreases along with the increase of the lattice constant c , as shown in Fig. 3(b). In fact, we also calculate the effective piezoelectric constant of the nanowires with bulk lattice constant c , and the results [also shown in Fig. 3(a)] indicate a monotonous decreasing dependence of e_{33}^a on the radius of nanowires. From Fig. 3(a), we can also see that the difference of e_{33}^a between nanowires D and E with the lattice constant c , relaxed or fixed, is very small, suggesting that larger nanowires will have similar e_{33}^a as nanowire E.

To summarize, we have carried out comprehensive first-principles studies on [0001] ZnO nanowires. The band gaps of ZnO bare nanowires increase along with the decrease of the radius of nanowires since the quantum confinement effect instead of the surface state plays an important role. Our calculations indicate that the effective piezoelectric constant e_{33}^a of ZnO nanowires is larger than that of bulk ZnO, and e_{33}^a is saturated when the diameter of nanowires is larger than 2.8 nm. In addition, we find a nontrivial dependence of the electromechanical coupling of ZnO nanowires on the radius as a result of the competition between two opposite factors. Our calculations address some key issues of ZnO nanowires, and our results support the application of ZnO nanowires and other related nanomaterials as nanosensors and nanoactuators.

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