PHYSICAL REVIEW B **80**, 201304(R) (2009)

Surface-induced polarity inversion in ZnO nanowires

Giancarlo Cicero[*]
Materials Science and Chemical Engineering Department, Politecnico of Torino, Torino, Italy
and CNR–IMEM, Parco Area delle Scienze 37A, I-43100 Parma, Italy

Andrea Ferretti[†]
Dipartimento di Fisica, Università di Modena e Reggio Emilia, I-41100 Modena, Italy
and National Center on nanoStructures and bioSystems at Surfaces, CNR–INFM–S3, Via Campi 213/a, I-41100 Modena, Italy

Alessandra Catellani
CNR–IMEM, Parco Area delle Scienze 37A, I-43100 Parma, Italy

(Received 6 October 2009; published 2 November 2009; publisher error corrected 3 March 2010)

In this work we use *ab initio* calculations to address the polar behavior of ZnO nanowires. Moving from a description based on Wannier functions, we employ a computational approach that allows one to express the polarization of a nanostructure in terms of local contributions. In particular, we discuss the changes in the nanostructure polarity in terms of two contributions, one related to changes in the equilibrium lattice parameters and the other related to surface effects. The former contribution is also interpreted on the basis of piezoelectric constants. Surprisingly, we find that for the smallest nanostructures, the average dipole is opposite to that of an infinite bulk structure.

DOI: 10.1103/PhysRevB.80.201304 PACS number(s): 73.22.−f, 61.46.Km, 71.15.Mb

Understanding how the properties of a material change when it is reduced to a nanostructure is important for a wide range of scientific and technological applications as well as for basic science. Until now the study of confinement effects has been mostly devoted to describe how the electronic properties of a material change in terms of band gap,[1] optical properties,[2,3] and electronic transport,[4] yet the effect of confinement on many other physical quantities is totally unexplored. In this Rapid Communication, we discuss how polarization changes in nanostructured materials, by employing a generalization of the local analysis proposed by Wu *et al.*[5] This approach allows one to decompose the intrinsic electrostatic potential of a nanostructure in terms of local dipole (LD) contributions and to address the mascroscopic polarity of the system at the same time. We have chosen to focus on ZnO, which is stable in the wurtzite (hexagonal) structure (WZ), is pyroelectric and presents one of the largest piezoelectric responses. Moreover, the growth of ZnO nanostructures is one of the most active fields in nanotechnology:[6] the most common structures are nanowires (NWs) grown along the polar [0001] axis and presenting nonpolar $(1\bar{1}00)$ lateral surfaces.[7] ZnO nanostructures have been recently employed in a wide range of applications, such as piezogenerators,[8,9] dye sensitized solar cells,[7] and gas sensors.[10]

We study the polarity of ZnO NWs of different diameters (see insets in Fig. 1), starting from a description of the electronic density in terms of maximally localized Wannier functions (WFs).[11] Our calculations predict that because of the large lattice relaxation and of charge rearrangements occurring at the NW surfaces, the average dipole of small NWs is strongly reduced with respect to what one could extrapolate from bulk behavior. Moreover, at diameters smaller than $\simeq 20$ Å we find that the surface dipoles counterbalance the bulk spontaneous polarization field.

According to the modern theory of polarization,[12,13] the macroscopic polarization of a crystal can be defined only with respect to a reference system and can be written, in terms of Wannier functions, as

$$\Delta P = P - P_{\mathrm{ref}} = \frac{e}{\Omega}\sum_{I} Z_I \Delta \mathbf{R}_I - \frac{2e}{\Omega}\sum_{i} \Delta \mathbf{r}_i^W, \qquad (1)$$

where Ω is the volume of the unit cell, $\mathbf{r}_i^W$ the WF centers, and $\mathbf{R}_I$ the ionic positions. For a periodic structure, ΔP is

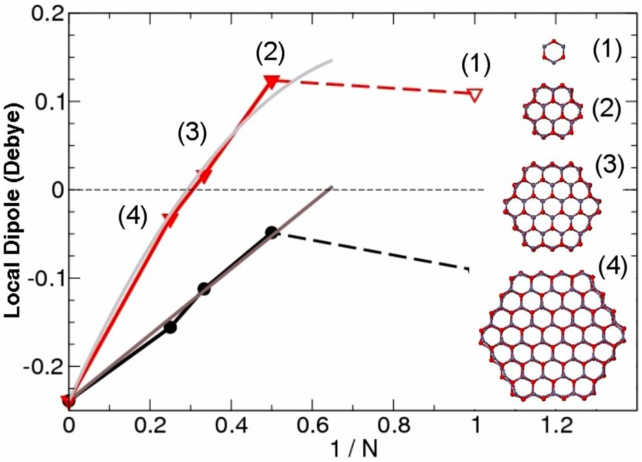

FIG. 1. (Color online) Local dipole analysis in ZnO NWs as a function of the size (N=shells that constitute the wire). The black curve (circles) corresponds to the behavior of several ZnO bulk system constrained at the lattice parameters c and a' obtained for the NWs (see Table I). The solid dark curve is a linear fit of these data. The red curve (triangles) represents the average LD (D) of the four NWs considered (shown as insets). The solid light line (gray) is a fitting of these data following Eq. (5). The points at the right of the graph have been connected with dashed line because they correspond to the smallest diameter (bulkless) NW.

1098-0121/2009/80(20)/201304(4)

defined modulo $2e\mathbf{R}_l/\Omega$, with $\mathbf{R}_l$ being a direct lattice vector.[14] In the case of a WZ bulk structure, the standard reference is zinc blende (ZB), which can be chosen to have null spontaneous polarization by symmetry.[15,16]

In order to apply the above approach to structures periodic only in one or two dimensions (e.g., NWs and surfaces), one should define a proper normalizing quantity (e.g., a length or a surface area). However, this would result in loss of generality in the comparison between different structures, with different dimensionalities. We thus use a scheme that passes through a normalization in terms of number of formula units per supercell (a ZnO pair in the case of zinc-oxide nanosystems) without loss of generality. In particular, we take advantage of the WFs approach that allows one to define *local* contributions to the average dipole in a system (at the price of an increased computational load due to the need of localizing WFs). In the following we will therefore refer to (variation of) LD. Focusing on the LDs, one can follow in principles the transformation of each WFs from the reference system, and the LD quantum is $2e\mathbf{R}_l$.

The local contributions are calculated by partitioning the WF set and the ionic charges into neutral units (here Zn-O pairs)[17] in such a way to obtain zero polarization for the reference bulk ZB phase structure. The total dipole/cell is obtained as the sum of these local contributions. Such procedure provides for the WZ phase of ZnO a local dipole of −0.24 D, which corresponds to a value of spontaneous polarization of $P^0 = -0.03\ \mathrm{C/m^2}$.[18] A similar approach has also been used in Ref. 19. The proposed scheme allows one to analyze how polarity varies in different parts of a structure (e.g., inner vs outer layers), thereby being able to define bulk and surface contributions when dealing with nanostructures. In the following we discuss few applications.

All the calculations were performed using the (ultrasoft) pseudopotential plane-wave implementation of density-functional theory (DFT) (Quantum-ESPRESSO code[20]). WFs of the bulk and nanostructured systems were computed using WANT.[21] The generalized gradient approximation Perdew-Burke-Ernzerhof[22] exchange-correlation functional was adopted.[23]

Extended surfaces. We have first considered a flat ZnO $(1\bar{1}00)$ nonpolar surface. The bulk polarization is parallel to the surface plane along the [0001] direction, yet the behavior may be completely different from what expected, due to surface relaxation. Indeed, this has been recently shown for α-SiC (Ref. 19) nonpolar surfaces. In our relaxed 1×1-$(1\bar{1}00)$ surface, ZnO bonds are shorter than in bulk (1.87 instead of 2.01 Å) and slightly tilted, with the Zn atom relaxing inward of about 0.3 Å. This atomic relaxation induces electronic charge density rearrangements characterized by charge transfer from Zn to the O atom, which ultimately determines changes in surface dipoles. Such charge transfer is highlighted by the analysis of the electron density of the highest occupied (HO) state which evidences a density accumulation on the surface O (see Fig. 2). These structural and electronic properties are in good agreement with previous DFT calculations.[24] The LD analysis as a function of the distance of the ZnO pair from the surface is reported in Fig. 2. The left panel shows that the bulk LD value [−0.24 D (Ref. 18)] is recovered at the third ZnO bilayer, i.e., beyond ≃4–5 Å from the surface. The most remarkable feature is that the LDs in the last two surface layers are opposite with respect to the bulk, due to atomic relaxation.

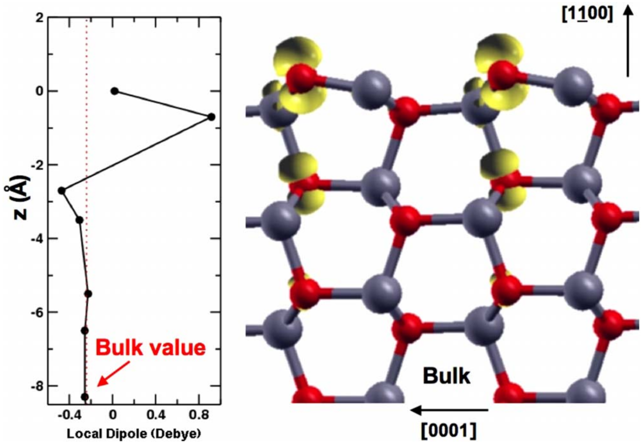

FIG. 2. (Color online) Left side: local dipole analysis in the direction perpendicular to the $(1\bar{1}00)$ surface; each point corresponds to a ZnO layer at increasing distance from the surface. Right side: ball and sticks rendering of the side view of ZnO $(1\bar{1}00)$ surface; small red/dark gray (big gray) spheres represent oxygen (zinc) atoms. The isosurface represents the charge density corresponding to the HOMO state of the system.

Nanowires. We have then considered ZnO NWs of increasing diameter in the range ≃4 to 23 Å which are represented in the insets of Fig. 1. These NWs have hexagonal shape (being made of N hexagonal shells, $N=1,\ldots,4$) and present non polar $(1\bar{1}00)$ facets, in agreement with experimental observation.[7] Two main relaxation mechanisms occur: The lattice parameter along the NW axis changes with respect to the bulk value and the atoms at the NW surfaces

TABLE I. Structural parameters of the relaxed NWs: In the first row **N** is the number of hexagonal shells of the NWs, **c** represents the lattice periodicity along the NW axis, while **a′** has been obtained by relaxing a ZnO bulk system with c constrained at equilibrium values for the NWs; **d** [Å] is the average diameter of the ZnO NWs.

	Bulk	NW4	NW3	NW2	NW1
N	∞	4	3	2	1
d [Å]	∞	23.0	16.5	9.9	3.8
c [Å]	5.315	5.361	5.385	5.423	5.397
a′ [Å]	3.289	3.280	3.276	3.269	3.274

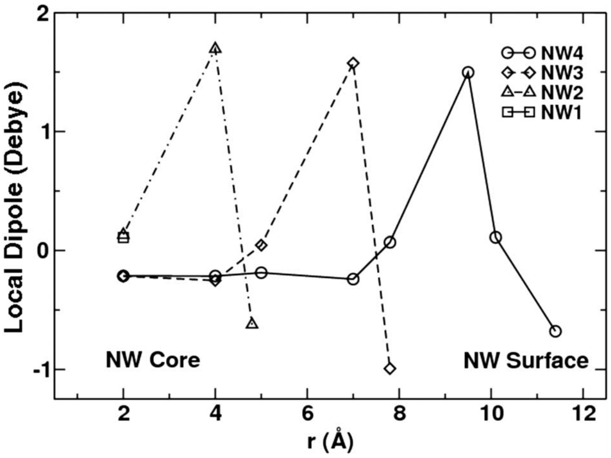

FIG. 3. Radial LD analysis in ZnO NWs of increasing diameter: each point represents the average LD in concentric shells at increasing distance from the NW center located an the zero of the abscissa axis.

relax. The lattice constant c along the NW axis increases decreasing the NW diameter and, except for the smallest diameter NW ($N=1$), the behavior appears to be linear. The anomalous behavior of the smallest NW is due to the fact that this NW has no bulklike ZnO pairs: None of its atoms is fourfold coordinated. While the NWs elongate along the c direction,[25] the lattice parameters along the perpendicular directions ($a=b$) shrink, since ZnO has a positive Poisson ratio ($\nu=-\epsilon_1/\epsilon_3$) for a strain applied along the c axis. The NW surfaces present a relaxation mechanism which is very similar to what observed for extended surfaces. In particular we find that the ZnO bonds at the surface are about 1.88 Å and slightly tilted. The charge rearrangement at the NW surfaces is also consistent with what observed for an infinite $(1\bar{1}00)$ surface: the HO orbital appears to be a surface state characterized by charge accumulation on the surface O atoms.

From the above description of the NW relaxation mechanism, one can anticipate that the change in polar behavior in a NW can be split into two contributions: (*i*) relaxation of lattice parameters, (*ii*) change in surface dipoles following atomic relaxation. The first contribution (Fig. 1, circles) can be estimated by calculating the LD in a strained bulk structure at the relaxed lattice parameters (c) of the NWs: this represents the effect of relaxation in the NW core, that leads to a strong decrease in spontaneous polarization ($P=N_{\mathrm{P}}D/\Omega$, with N_{P} being the number of LD's per cell, D the LD value, and Ω the volume of the cell).

The average dipoles of the ZnO NWs that we calculated in our simulations are indicated by red triangles in Fig. 1. Since these values were obtained as averages over the whole nanostructures, they represent the convolution of the two effects described above: the strained bulk effect, and the surface effects. It is evident that the change in LD of all the NWs is larger than what can be estimated by considering only changes in lattice parameters (black circles). In all cases the surface relaxation causes a further decrease (in modulus) of the nanostructure average dipole and can even determine a sign inversion: the LD component parallel to the NW axis becomes positive for NWs with diameter smaller than $\simeq 20$ Å.

The contribution of *lattice relaxation* to the total polarization can be described in terms of piezoelectric coefficients. The LD in the core of the NWs are lower than the equilibrium bulk term because, as stated before, while elongating along the c axis, the bulk structure shrinks in the perpendicular directions. By using the definition of Poisson ratio and considering that $\epsilon_1=\epsilon_2$, the change in spontaneous polarization in a strained bulk is given by

$$P-P^0=2e_{31}\epsilon_1+e_{33}\epsilon_3=(e_{33}-2e_{31}\nu)\epsilon_3, \qquad (2)$$

where P^0 is the equilibrium structure polarization, e_{31} and e_{33} are the piezoelectric constants and ϵ_i are the strains along the three lattice directions. The value of the effective piezoelectric constant $(e_{33}-2e_{31}\nu)$ from our calculations is $1.29\ \mathrm{C/m^2}$. The effective piezoelectric constant is positive and larger than the bulk value e_{33} (we get $e_{33}=1.04\ \mathrm{C/m^2}$, $e_{31}=-0.44\ \mathrm{C/m^2}$, while $P^0=-0.03\ \mathrm{C/m^2}$, in agreement with the values reported in Ref. 26) indicating that the spontaneous polarization (and correspondingly the LD) will strongly decrease in modulus in a relaxed nanostructure. As said above, the black circles in Fig. 1 represent this behavior and correspond to the change in LD that a NW would experience if only bulk contributions would be relevant.

To highlight the *role of surfaces*, one can perform a LD analysis in the radial direction of the NWs (see Fig. 3). The four sets of data represent the average LD in hexagonal shells at increasing distance from the NW axis, which is located at the origin of the plot. The NW cores with $N=1,2$ do not present any bulklike ZnO pairs, that instead appear in the cores of NWs with $N=3,4$. In all the cases, the largest changes occur at the surface and subsurface layers: the qualitative features of the external shells of the three bigger NWs are similar and resemble that of the infinite $(1\bar{1}00)$ surface (compare with Fig. 2).

Scaling model. The effects of lattice and surface relaxation on the NW polar behavior can be expressed by an analytical formula that accounts for the surface/volume scaling at varying NW size. We write the average LD as a bulk contribution, $D^0(N)$ (as if all the ZnO pairs would have the same dipole as in the reference bulk), plus a surface correction (D_{Surf}),

$$D_{\mathrm{P}}(N)=D_{\mathrm{Surf}}+N_{\mathrm{P}}(N)D^0(N), \qquad (3)$$

where N is the number of shells in the NWs, proportional to the diameter, and $N_{\mathrm{P}}(N)=6N^2$ is the number of ZnO pairs in the NWs. First we assume that the surface term can be written as $D_{\mathrm{Surf}}(N)=N_{\mathrm{Surf}}(N)\gamma_S$, where γ_S is a constant value for all the wires and $N_{\mathrm{Surf}}(N)=24(N-1)$ is the number of pairs in the two outermost shells (surface). Second, we assume a linear scaling of the lattice (piezo) contribution with respect to $1/N$, according to

$$D^0(N)=D_B^0+D^1\frac{1}{N}, \qquad (4)$$

Using the above expressions to write $D_{\mathrm{P}}(N)/N_{\mathrm{P}}(N)$ (i.e., the average LD in the NWs) leads to

$$D=D_B^0+(D^1+4\gamma_S)\frac{1}{N}-4\gamma_S\frac{1}{N^2}. \qquad (5)$$

The linearity of Eq. (4) is well reproduced by our data (circles in Fig. 1) and the fitting is reported as the dark solid line in the same figure. The fit for the wires is given by the light solid line (gray), which is obtained by Eq. (5) using $D_B^0=-0.239$ D, $D^1=0.373$ D, and $\gamma_S=0.157$ D. The first two values are taken from the linear fit of Eq. (4), while the surface term γ_S is directly fitted on the data for the NWs (triangles). Since we fixed D^0 and D^1, this is a one-parameter fit. Besides defining the scaling law of the average dipole for NWs, this simple representation allows one to grasp immediately the contribution of the surface in a nanostructure, and to evaluate the minimal dimensions to recover a bulklike behavior.

In conclusion, in this work we have shown that the polarization behavior of a material critically depends on the size extension of the structure considered; for the particular case of WZ NWs we prove the existence of a minimum diameter below which the nanostructure polarity is inverted with respect to the bulk one. For ZnO NWs grown along the [0001] direction we have found that the critical diameter is about 20 Å. We have rationalized our results in terms of two contributions, one due to lattice relaxation occurring in a nanostructure and the other related to surface effects. The change in sign of the polarity is mostly determined by the second effect, which becomes dominant at small diameters because of the large surface/volume ratio. It is possible that the present results overestimate the experimental data, that can be affected by the specific local environment such as inclusion of defects, or saturation of dangling bonds via adsorption of chemical species.

We acknowledge funding from MIUR through FIRB LATEMAR (2005–2009) and PRIN Cofin (Grant No. 2006022847). This work is also part of the NanoLICHT project supported by "NanoSci-ERA: NanoScience in the European Research Area" (EU-FP6). Computer time was provided by the Jülich Supercomputing Centre and by CINECA through the CNR-INFM "Iniziativa Calcolo Parallelo." We thank J. C. Grossman (MIT, Cambridge, MA) for useful scientific discussions.

---

*Corresponding author; giancarlo.cicero@polito.it

†Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA.

[1] W. E. Buhro and V. L. Colvin, Nature Mater. **2**, 138 (2003).

[2] V. I. Klimov, S. A. Ivanov, J. Nanda, M. Acherman, I. Bezel, J. A. McGuire, and A. Piryatinski, Nature (London) **447**, 441 (2007).

[3] S. A. Empedocles and M. G. Bawendi, Science **278**, 2114 (1997).

[4] A. I. Yanson, G. R. Bollinger, H. E. van den Brom, N. Agrait, and J. M. van Ruitenbeek, Nature (London) **395**, 783 (1998).

[5] X. Wu, O. Diéguez, K. M. Rabe, and D. Vanderbilt, Phys. Rev. Lett. **97**, 107602 (2006).

[6] Z. L. Wang, J. Phys.: Condens. Matter **16**, R829 (2004).

[7] M. Law, L. E. Green, J. C. Johnson, R. Saykally, and P. Yang, Nature Mater. **4**, 455 (2005).

[8] Y. Qin, X. Wang, and Z. L. Wang, Nature (London) **451**, 809 (2008).

[9] J. Song, J. Zhou, and Z. Wang, Nano Lett. **6**, 1656 (2006).

[10] E. Comini, C. Baratto, G. Faglia, M. Ferroni, and G. Sberveglieri, J. Phys. D **40**, 7255 (2007).

[11] N. Marzari and D. Vanderbilt, Phys. Rev. B **56**, 12847 (1997).

[12] D. Vanderbilt and R. D. King-Smith, Phys. Rev. B **48**, 4442 (1993).

[13] R. Resta, Rev. Mod. Phys. **66**, 899 (1994).

[14] It is important to observe that in order to eliminate ambiguity on the sign of ΔP, this has to be much smaller than the *"modulo,"* otherwise one has to follow the transformation from the reference structure explicitly.

[15] L. D. Landau and E. M. Lifschitz, *Electrodynamics of Continuous Media* (Pergamon, Oxford, 1960).

[16] R. M. Martin, Phys. Rev. B **9**, 1998 (1974).

[17] In ZnO, the LD can be expressed as the sum of a contribution centered on the Zn atom and the other on the O. The dipole on the Zn arises from the five occupied *d* orbitals (5 WFs and Z_I =+10e), the dipole on the O is calculated by considering the closest 4 *sp* WFs and the four neighboring Zn atoms.

[18] This value is consistent with -0.032 C/m^2, that we obtained to the same level of accuracy on eigenvectors by means of the Berry Phase approach.

[19] G. P. Brandino, G. Cicero, B. Bonferroni, A. Ferretti, A. Calzolari, C. M. Bertoni, and A. Catellani, Phys. Rev. B **76**, 085322 (2007).

[20] P. Giannozzi *et al.*, J. Phys. Condens. Matter **21**, 395502 (2009).

[21] A. Ferretti, B. Bonferroni, A. Calzolari, and M. Buongiorno Nardelli, WANT code, http://www.wannier-transport.org (2007).

[22] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[23] Wave functions (density) are expanded up to a cutoff energy of 28 (280) Ry. For surface calculations we adopted (1×1) slabs including up to 16 ZnO layers and a 10 Å vacuum thickness, with $6\times6\times1$ and $12\times12\times1$ **k**-point sampling for relaxation and WFs respectively. The NWs are periodic along the polar [0001] axis, and we include a vacuum region between periodic replicas not thinner than $\simeq 10$ Å. For NWs we adopted a **k** point of $1\times1\times6$ and $1\times1\times12$ for relaxation and calculation of WFs. All the structures were fully relaxed until the forces acting on the atoms were less than 10^{-3} Ry/bohr.

[24] B. Meyer and D. Marx, Phys. Rev. B **67**, 035403 (2003).

[25] The maximum elongation $[\epsilon_3=(c-c_0)/c_0]$ is observed for the nanowire with $N=2$ (diameter of ~ 9 Å) and its value is about $\epsilon_3=+0.02$: in a bulk system such strain would correspond to an applied stress of about 3 GPa.

[26] U. Özgür, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho, and H. Morkoç, J. Appl. Phys. **98**, 041301 (2005).