

ADVANCED MATERIALS

Supporting Information

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Piezo-Semiconductive Quasi-1D Nanodevices with or without Anti-Symmetry

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SUPPLEMENTARY INFORMATION

Piezo-semiconductive quasi-1D nanodevices without anti-symmetry

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Statement of the problem

We consider of a ZnO nanowire (NW) grown along the c -axis on a substrate. The wire is normally compressed by a vertical force $\mathbf{f} = -f_z \mathbf{z}_0$ exerted at the top. Previous results^[1] indicated that when the free charge carrier density is accounted for, the compressed tip of the NW shows a negative open-circuit potential (called piezopotential).

The elastic behavior of piezoelectric media is governed by Newton's law^[2]

$$\nabla \cdot \boldsymbol{\sigma} = 0, \quad (1)$$

while the piezopotential is governed by the semiconductor device equation^[3]

$$\nabla \cdot \mathbf{D} = q \left(N_D^+ + p - N_A^- - n \right). \quad (2)$$

Equations (1)-(2) are fully coupled by the constitutive equations relating mechanical and electrical quantities in piezoelectric media.

According to the Fermi-Dirac statistics, the carrier densities n and p in Equation (2) are determined under thermodynamic equilibrium by the position of the Fermi level \mathcal{E}_F with respect to the conduction and valence band edges \mathcal{E}_c and \mathcal{E}_v , respectively. The carrier densities can thus be calculated as

$$n \cong N_c \exp\left(\frac{\mathcal{E}_F - \mathcal{E}_c}{k_B T}\right), \quad (3a)$$

$$p \cong N_v \exp\left(\frac{\mathcal{E}_v - \mathcal{E}_F}{k_B T}\right) \quad (3b)$$

where

$$N_v = 2 \left(\frac{2\pi m_h k_B T}{h^2} \right)^{\frac{3}{2}} \quad (4a)$$

$$N_c = 2 \left(\frac{2\pi m_e k_B T}{h^2} \right)^{\frac{3}{2}} \quad (4b)$$

are the effective density of states in the valence and conduction bands, respectively. In Equations (3)-(4) T is the absolute temperature, k_B the Boltzmann constant, h the Planck constant, m_e the effective mass of conduction band electrons, and m_h the effective mass of valence band holes.

Strictly, when impurities are introduced in semiconductor crystals, not all dopants (N_A or N_D) are necessarily ionized, depending on the impurity energy level and the lattice temperature. In particular, the ionized concentrations are given by

$$N_A^- = \frac{N_A}{1 + g_A \exp\left(\frac{\mathcal{E}_A - \mathcal{E}_F}{k_B T}\right)} \quad (5)$$

$$N_D^+ = \frac{N_D}{1 + g_D \exp\left(\frac{\mathcal{E}_F - \mathcal{E}_D}{k_B T}\right)}, \quad (5)$$

where g_A and g_D are the ground-state degeneracy of the acceptor and donor impurity levels (usually $g_A = g_D = 2$), while \mathcal{E}_A and \mathcal{E}_D are the energy of the states introduced by acceptors and donors.

The conduction \mathcal{E}_{c0} and valence \mathcal{E}_{v0} band levels of a free-standing undeformed NW can be computed with respect to the Fermi level \mathcal{E}_F (set to zero as reference), enforcing the neutrality conditions $N_D^+ + p = N_A^- + n$.

When the ZnO NW is compressed, the redistributions of mobile electrons and holes under thermodynamic equilibrium are given by the Fermi-Dirac statistics where the valence and conduction band levels become functions of the spatial coordinate \mathbf{x} , i.e., $\mathcal{E}_v(\mathbf{x})$ and $\mathcal{E}_c(\mathbf{x})$.

In particular, the band edge shift $\Delta\mathcal{E}(\mathbf{x})$ is the sum of the electrostatic energy term qV and the deformation potential term ΔE_{def} (that may be important for large strains), i.e.

$$\Delta\mathcal{E}(\mathbf{x}) = \mathcal{E}_c(\mathbf{x}) - \mathcal{E}_{c0} = \mathcal{E}_v(\mathbf{x}) - \mathcal{E}_{v0} = -qV + a_{\text{def}} \frac{\Delta v}{v_0}, \quad (6)$$

where V is the electrostatic potential, and $a_{\text{def}} \frac{\Delta v}{v_0}$ is the band-edge shift due to the

deformation (which is proportional to the relative volume change $\frac{\Delta v}{v_0}$ through the

deformation potential constant a_{def}). Finally, also the activation process of donors and

acceptors is modified by the deformation of the conduction and valence band edge. In fact, in

Equation (6) the acceptor energy level is given by $\mathcal{E}_A(\mathbf{x}) = \mathcal{E}_v(\mathbf{x}) + \Delta\mathcal{E}_A$, while the donor

energy level reads $\mathcal{E}_D(\mathbf{x}) = \mathcal{E}_c(\mathbf{x}) - \Delta\mathcal{E}_D$ (the band gap energy \mathcal{E}_g is assumed to remain constant).

Numerical solution

The piezoelectric-semiconductor equations constitute a coupled nonlinear set. In general, it is not possible to obtain a solution directly in one step, but rather a nonlinear iteration method must be used. As concerns the choice of independent variables, the coupled electro-mechanical problem is solved for the variables (\mathbf{u}, V) where \mathbf{u} is the displacement vector in the spatial description (Eulerian form). As a consequence, the electric field is related to the electrostatic potential by $\mathbf{E} = -\nabla V$, while the mechanical strain vector is related to the mechanical displacement by $\boldsymbol{\varepsilon} = \frac{1}{2}(\nabla\mathbf{u} + \nabla\mathbf{u}^T)$. By introducing the independent variables (\mathbf{u}, V) , Equations (1)-(2)-(3) can be rewritten to obtain the coupled nonlinear partial differential equations as

$$\nabla \cdot \left\{ [\mathbf{c}^E][\mathbf{B}]\mathbf{u} + [\mathbf{e}]^T \nabla V \right\} = 0 \quad (7a)$$

$$\nabla \cdot \left\{ [\mathbf{e}][\mathbf{B}]\mathbf{u} - \kappa_0 [\boldsymbol{\kappa}^\varepsilon] \nabla V \right\} = q \left[N_D^+ + p - N_A^- - n \right], \quad (7b)$$

where the impurities and the mobile charge densities are linked to the electrical potential V and the displacement \mathbf{u} . In order to make the solution of Equations (7) more efficient and to avoid possible numerical overflow and underflow errors, we performed calculations using normalized quantities through a consistent scaling.

The system in Equations (7) has been solved through a standard Finite Element Method in conjunction with the damped iterative Newton method to deal with the nonlinearity. Taking advantage of the rotational (cylindrical) symmetry of the structure, we reduced to a 2.5-D problem^[4] (i.e. our 3D problem can be simulated in a simplified manner due to the presence

of some symmetries) by restricting the computational domain to a transverse rz -plane imposing equal to zero any derivative with respect to the angular variable φ . A nodal approach with third-order Lagrangian basis functions defined on a planar triangular mesh has been used.

The symmetric 6×6 stiffness matrix $[\mathbf{c}^E]$ of ZnO theoretically requires 21 independent coefficients. However, because of the symmetries in wurtzite hexagonal crystals, the stiffness independent coefficients reduce to 6. Though an isotropic model has been shown a good approximation in some cases, we have also considered the anisotropic model and verified that even in our cases the differences with isotropic model are minor.

The polarization field produced by the strain through the piezoelectric effect is described by the piezoelectric tensor $[\mathbf{e}]$, which theoretically has 18 independent coefficients. Due to crystal symmetries in hexagonal wurtzite phase there remain only three independent components.^[5] It can be observed that for a pure compression or traction, the resulting piezoelectric field is oriented along the NW growth axis. As concerns the dielectric relative permittivity tensor, it presents a diagonal form.^[6] The ZnO band gap energy \mathcal{E}_g has been assumed equal to 3.4 eV which is so large that the contribution of holes with n -type doping and of electrons with p -type doping are negligible.

Numerical values of the physical parameters used in the simulations

The geometrical parameters of the nanowire are $R_{\text{nw}} = 150 \text{ nm}$ and $L_{\text{nw}} = 4 \mu\text{m}$.^[7] The stiffness constants of ZnO are (all the symmetries are not indicated for conciseness)

$c_{1111}^E = 209.7 \text{ GPa}$, $c_{3333}^E = 210.9 \text{ GPa}$, $c_{1122}^E = 121.1 \text{ GPa}$, $c_{2233}^E = 105.1 \text{ GPa}$,
 $c_{2323}^E = 42.47 \text{ GPa}$, $c_{1212}^E = 44.29 \text{ GPa}$;^[8] the piezoelectric constants are

$e_{311} = e_{322} = -0.51 \text{ [C/m}^2\text{]}, e_{333} = 1.22 \text{ [C/m}^2\text{]}, e_{113} = e_{223} = -0.45 \text{ [C/m}^2\text{]}$; [5] the dielectric relative permittivity constants are $\kappa_{11}^\varepsilon = \kappa_{22}^\varepsilon = 7.77$ and $\kappa_{33}^\varepsilon = 8.91$; [6] the effective electron mass is $m_e = 0.28m_0$, [9] with m_0 the free-electron mass; the deformation potential constant is $a_{\text{def}} = -6.05 \text{ eV}$; [10] the distance between the donor (acceptor) energy level and conduction (valence) band is $\Delta\mathcal{E}_D = \Delta\mathcal{E}_A = 35 \text{ meV}$; the temperature is $T = 300 \text{ K}$; the band gap is $\mathcal{E}_g = 3.4 \text{ eV}$.

Supporting results

For completeness, Figure S1 shows the carrier concentration along the axis of a cylindrical nanowire (radius 150 nm and length 2 μm) for typical doping concentrations under a 442 nN [7] compressive force; when reducing the doping levels under constant compressive force, the depletion/accumulation regions broaden.

Though practical nanowires, even in absence of intentional doping, unavoidably show some equivalent doping level (e.g. due to crystal imperfections and impurities), it is interesting to consider, as limiting cases, very low doping levels and even an hypothetical purely dielectric ZnO nanowire. Figure S2 shows the piezopotential for a cylindrical ZnO nanowire under axial compression ($F = -442 \text{ nN}$) for very low levels of n-type doping ranging from 10^{11} cm^{-3} to 10^{16} cm^{-3} and for the case of a purely dielectric ZnO nanowire. The results show that, under the above-mentioned compressive force, at doping levels as low as 10^{11} cm^{-3} the piezopotential is similar to that of the dielectric nanowire. Clearly, in the hypothetical dielectric ZnO nanowire, there are no depletion/accumulation regions at the tip/base and the voltage drop region extends to the whole nanowire.

The analysis of hypothetical perfectly insulating nanowires is much easier (only linear equations must be solved so that iterative methods are not required); however, such analysis is

useful because insulating nanowires can be considered as a limiting case (e.g., the piezopotential is obviously reduced by free charges) and because we may verify that the breaking-off of the anti-symmetrical dependence of the voltage drop on the compressive/tensile force is due to the coupling of the piezo-semiconductive equations. Figure S3a shows the z -component of the displacement in truncated dielectric conical nanowires with different tip radii (bottom radius 150 nm and length 2 μm). Since the structural parameters of the nanowire are fixed and the inverse piezoelectric effect is negligible, these displacements are practically identical to those reported in Figure 3a of the main paper. However, clearly, the piezopotentials (Figure 3b and S3b) are different because of the crucial effect of free charges; in particular, for the insulating case there are no accumulation/depletion regions at the tip/base and the voltage drop region extends to the entire nanowire. Figure S3c shows the electrostatic and mechanical energy and the ratio between electrostatic and total energies as a function of force; in striking contrast with the semiconductive case the parameter ξ is almost constant. Figure S3d shows the voltage difference between the tip and base of the insulating nanowires for tensile and compressive forces, thus confirming that the coupling of piezo-semiconductive equations is crucial for breaking the strain/force/pressure-voltage anti-symmetry.

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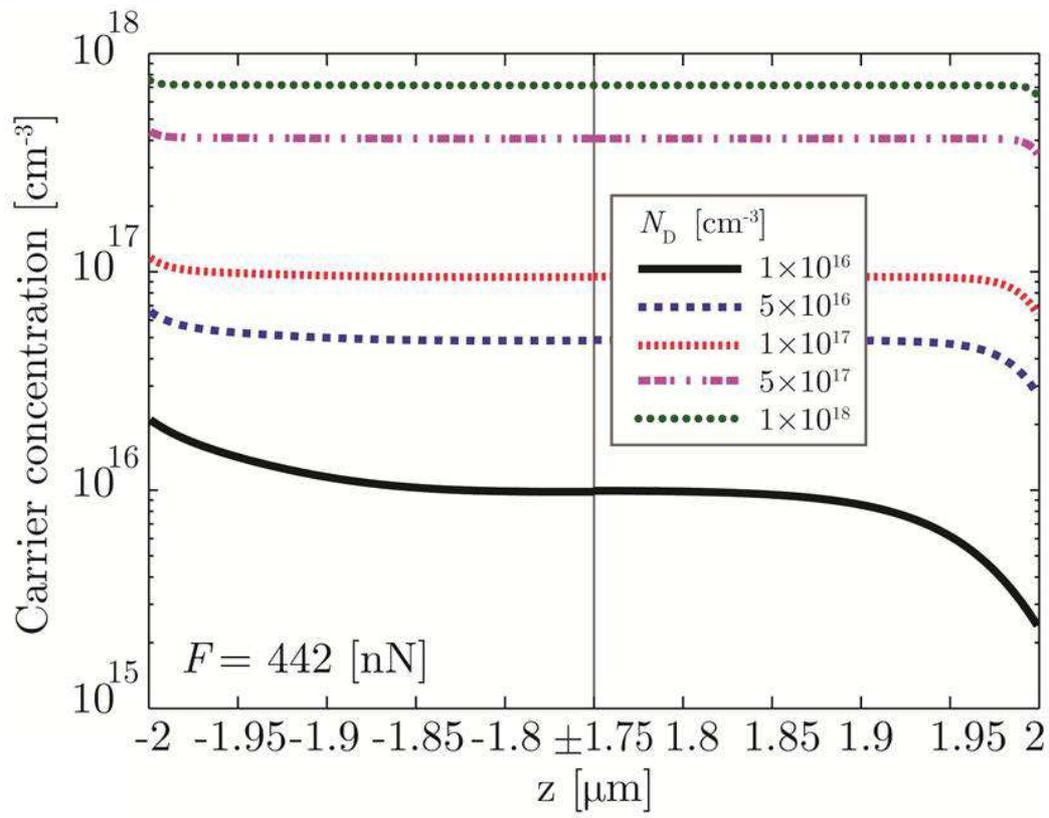


Figure S1. Carrier concentration along the axis of a cylindrical nanowire (radius 150 nm and length 2 μm) for different doping concentrations under a 442 nN^[12] compressive force.

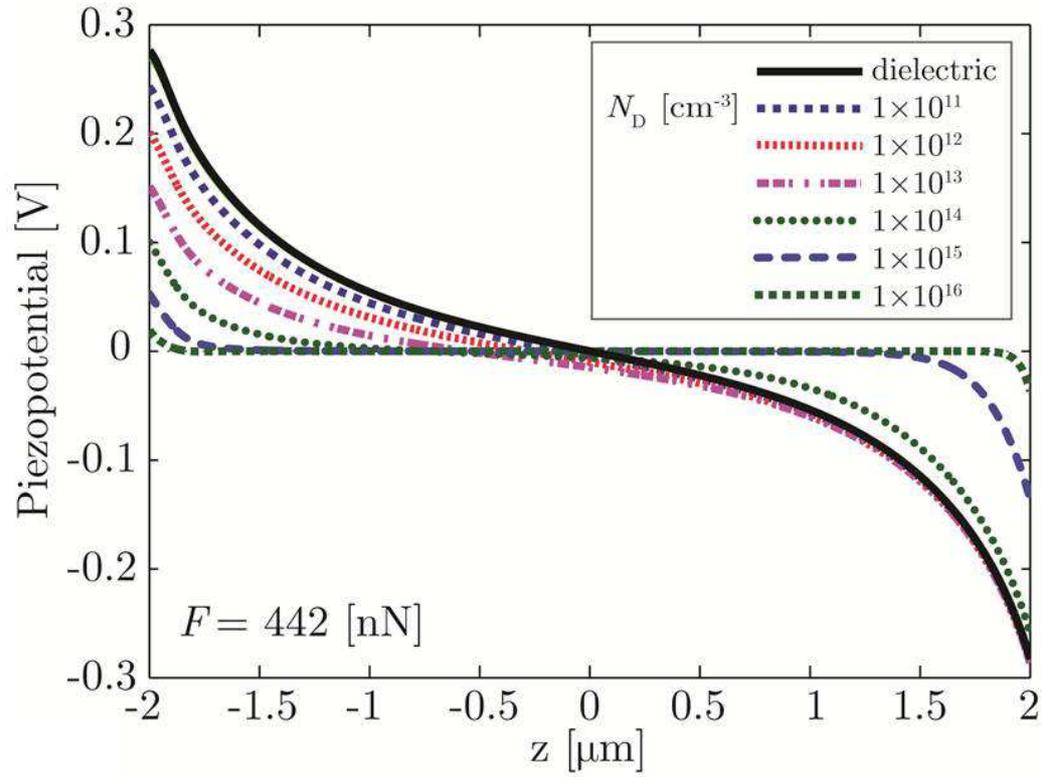


Figure S2. Piezopotential along the axis of a cylindrical nanowire (radius 150 nm and length 2 μm) for different doping concentrations and for the dielectric case under a 442 nN^[12] compressive force.

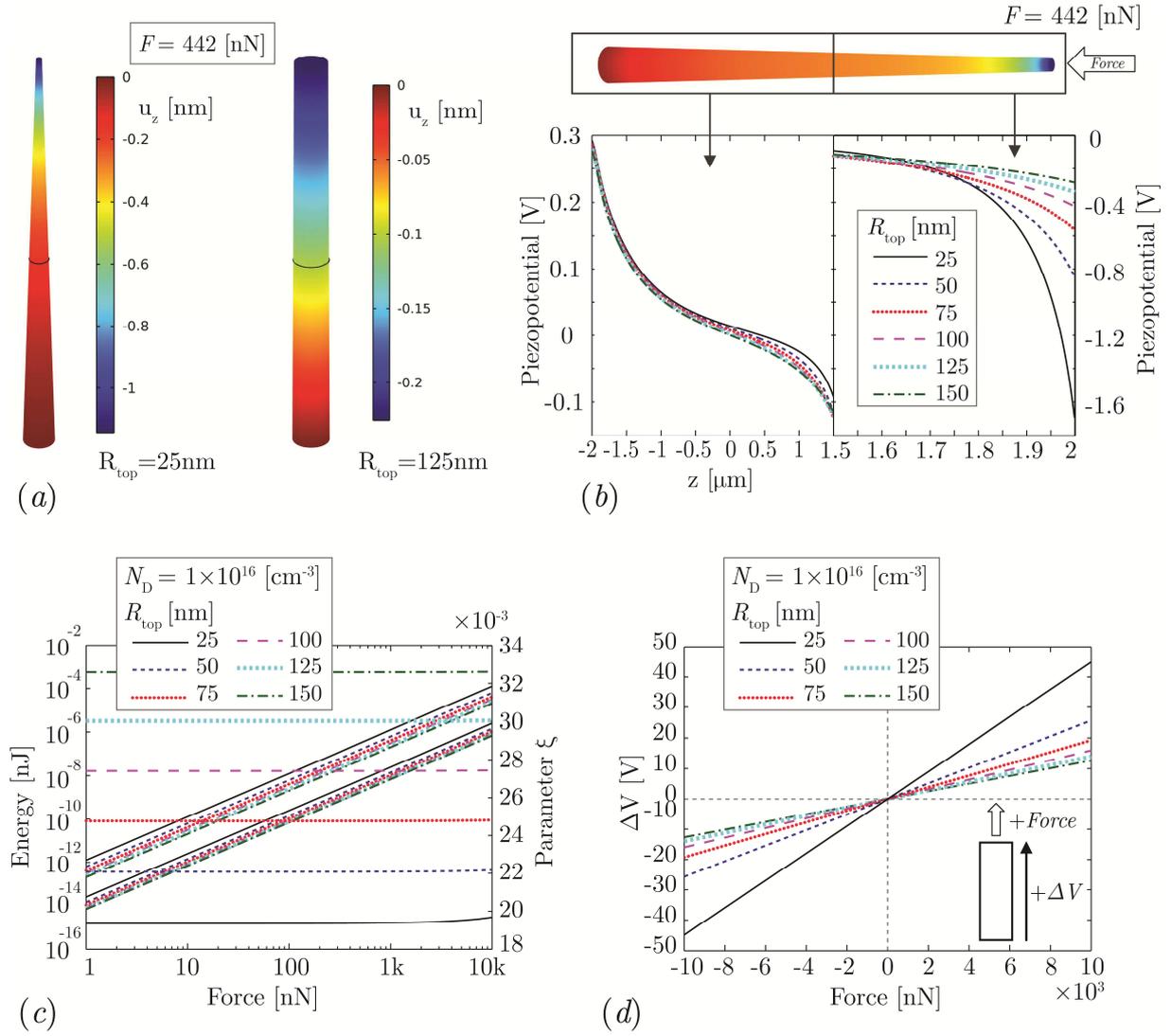


Figure S3. Conical dielectric nanowire (bottom radius 150 nm and length 2 μm) surrounded by free space and subject to compressive/tensile force. a) Displacement in truncated conical nanowires with different tip radii. b) Piezopotential at the base (left) and tip (right) of the truncated conical nanowires. c) Electrostatic, mechanical energy and ratio between electrostatic and total energies as a function of force. d) Voltage difference between the tip and base of the nanowire for tensile and compressive forces: as expected the anti-symmetry is always conserved in the dielectric case.