Photovoltaics with Piezoelectric Core-Shell Nanowires: Supplementary Information

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S-I Electro-elastically coupled continuum elasticity theory

We have performed computations for the elastic strain and piezoelectric field in III-V semiconductor core-shell nanowires (NWs) based on fully electro-elastically coupled continuum elasticity (CE) theory. In these computations we have taken into account the underlying material properties, such as the stiffness, piezoelectric and dielectric constants, and the nanowire geometry, such as material interfaces and surface faceting, and the crystal orientation with respect to the nanowire axis. We have also assumed that there are no free (external) charges in the systems.

The stress $\mathbf{T}$ and electric displacement $\mathbf{D}$ are related to the strain $\mathbf{S}$ and electric field $\mathbf{E}$ through the constitutive equation,¹

$$\begin{bmatrix} \mathbf{T} \\ \mathbf{D} \end{bmatrix} = \begin{bmatrix} \mathbf{C} & \mathbf{e}^T \\ \mathbf{e} & -\epsilon \end{bmatrix} \begin{bmatrix} \mathbf{S} \\ -\mathbf{E} \end{bmatrix}, \quad (1)$$

where $\mathbf{C}$ is the elastic stiffness tensor, $\mathbf{e}$ the piezoelectric tensor, and ϵ dielectric tensor.

The equilibrium electro-elastic structure of a core-shell NW is solved by a variation of the crystal energy using the finite element method. The crystal energy of a core-shell NW is given by the sum of the core (c) and shell (s) electro-elastic energies,

$$U = \frac{1}{2} \left\{ \int_c [(\mathbf{S} + \mathbf{S}_0)^T \cdot \mathbf{C}_c \cdot (\mathbf{S} + \mathbf{S}_0) + \mathbf{E}^T \cdot \epsilon \cdot \mathbf{E}] dV + \int_s [\mathbf{S}^T \cdot \mathbf{C}_s \cdot \mathbf{S} + \mathbf{E}^T \cdot \epsilon \cdot \mathbf{E}] dV \right\}, \quad (2)$$

where $\mathbf{C}_c$ and $\mathbf{C}_s$ stand for the elastic stiffness tensors of the core and shell materials. In the above equation, the misfit between the core and shell lattices has been introduced by a prestrain $\mathbf{S}_0 = (a_s - a_c)/a_s \cdot [111000]^T$ of the core material, where a_c and a_s are the lattice constants of the core and shell bulk materials, respectively. The same prestrain was used for both zinc-blende (ZB) and wurtzite (WZ) crystalline systems.

The elastic stiffness tensor of a ZB crystalline material is given by

$$\mathbf{C} = \begin{bmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{44} \end{bmatrix}, \quad (3)$$

where c_{ij} are the elastic stiffness constants of the considered ZB crystal. The corresponding piezoelectric tensor is given by

$$\mathbf{e} = \begin{bmatrix} 0 & 0 & 0 & e_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & e_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & e_{14} \end{bmatrix}, \quad (4)$$

where e_{14} is the piezoelectric constant of the ZB crystal. The dielectric tensor is given by

$$\epsilon = \epsilon_0 \begin{bmatrix} \epsilon & 0 & 0 \\ 0 & \epsilon & 0 \\ 0 & 0 & \epsilon \end{bmatrix}, \quad (5)$$

where ϵ_0 is the permittivity of vacuum and ϵ is the relative permittivity.

TABLE S1: Material parameters employed for InAs and InP in both the ZB and WZ phases. The ZB lattice constants a were obtained from Ref. [2] and the WZ lattice constants a and c were calculated from the ZB ones, assuming an ideal WZ lattice. The elastic stiffness constants were obtained from Ref. [3]. The piezoelectric and dielectric constants were obtained from Refs. [4] and [5].

Parameter	unit	InAs		InP	
		ZB	WZ	ZB	WZ
a (ZB)	[Å]	6.058		5.870	
a (WZ)	[Å]		4.284		4.151
c (WZ)	[Å]		8.567		8.301
c_{11}	[Pa]	0.922	1.103	1.095	1.311
c_{12}	[Pa]	0.465	0.428	0.557	0.513
c_{13}	[Pa]		0.321		0.386
c_{33}	[Pa]		1.209		1.438
c_{44}	[Pa]	0.444	0.273	0.526	0.321
c_{66}	[Pa]		0.338		0.399
e_{14}	[C m ⁻²]	-0.050		0.06	
e_{15}	[C m ⁻²]		0.040		0.071
e_{31}	[C m ⁻²]		-0.045		0.103
e_{33}	[C m ⁻²]		-0.028		0.086
ϵ		14.5		12.74	
ϵ_a			14.5		12.74
ϵ_c			14.5		12.74

The elastic stiffness tensor of a WZ phase material is on the contrary given by¹

$$\mathbf{C} = \begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66} \end{bmatrix}, \quad (6)$$

where c_{ij} are the elastic stiffness constants of the WZ material and $c_{66} = (c_{11} - c_{12})/2$. The piezoelectric coupling tensor is given by

$$\mathbf{e} = \begin{bmatrix} 0 & 0 & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{15} & 0 & 0 \\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 \end{bmatrix}, \quad (7)$$

where e_{ij} are the piezoelectric constants of the WZ material, and the dielectric tensor is given by

$$\boldsymbol{\epsilon} = \epsilon_0 \begin{bmatrix} \epsilon_a & 0 & 0 \\ 0 & \epsilon_a & 0 \\ 0 & 0 & \epsilon_c \end{bmatrix}, \quad (8)$$

with ϵ_a and ϵ_c being the relative permittivities along the a and c axes, respectively.

The material parameters used in our computations are summarized in Table S1. We have used an isotropic dielectric tensor with $\epsilon_a = \epsilon_c$ for the WZ phased materials. This is because of a big uncertainty in the theoretically predicted dielectric constants for InAs and InP in the WZ phase. Furthermore, ϵ_a plays a minor role for the considered axial (i.e., c -axis) piezoelectric polarization. Based on symmetry arguments we also expect ϵ_c of a WZ phase material to be the same as, or very close to, ϵ of the corresponding ZB phased material.

S-II Band edges of strained core-shell nanowires

We have computed the band edges of free, intrinsic, strained core-shell NWs in vacuum. As an example, Figure S1(a) shows the computed piezoelectric potential V_{PZ} at the center of the core along the NW axis for ZB crystalline InAs/InP core-shell NWs with different lengths. The core and shell radii are $r_c = 30$ nm and $r_s = 50$ nm, respectively. The lengths of the NWs are $L_z = 2r_s$, $4r_s$, and $6r_s$. We note that V_{PZ} acquires a constant gradient (along the NW axis)

FIG. S1: **Effective potential of electrons and holes in strained core-shell NWs.** (a) Piezoelectric potential, (b) conduction band edge energy, and (c) valence band edge energy in strained ZB core-shell NWs with a core of InAs and a surrounding shell of InP. The data were evaluated along the central axis of NWs with a core radius of $r_c = 30$ nm, outer shell radius of $r_s = 50$ nm, and lengths of $L_z = 2r_s$ (blue thick solid lines), $L_z = 4r_s$ (red long-dashed lines), and $L_z = 6r_s$ (black short-dashed lines). The band edge energies have been given with respect to the corresponding values in strain-free bulk InAs. The band edges at the ends of the NWs are expected to be further flattened by charge accumulations and/or Fermi-level pinning, which were not included in the calculations for the results presented in panels (b) and (c).

even in the interior of relatively short NWs. This gradient corresponds to an electrical field, which is comparable to a typical built-in field in a p-n junction diode.⁶

Figures S1(b) and S1(c) show the conduction and valence band edges at the center of the core along the NW axis, with respect to the band edges of bulk InAs. These band edges include the numerically computed piezoelectric potential and the strain-induced deformation potential.⁷ They do, however, not include any contributions from quantum confinement effects. The bulging of the end surfaces and the consequent release of the axial stress reduce the strain and, thus, the piezoelectric field close to the ends of the NWs. This is seen as flattening of the potential and band bendings in the vicinities of the NW ends in Figures S1(a)–S1(c).

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