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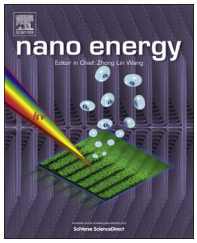

Non-linear piezoelectricity in wurtzite ZnO semiconductors

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Abstract
In this work we explore the strain dependence of the piezoelectric effect in wurtzite ZnO crystals. We write the polarization in terms of the internal anion-cation displacement, the ionic and dipole charges and use ab initio Density Functional Theory to evaluate the dependence of all quantities on the strain tensor. We determine that similar to III-V semiconductors the piezoelectric effect is non-linear in the strain tensor. We report the quadratic piezoelectric coefficients and a revised value of the spontaneous polarization. We find that in ZnO nanowires, the non-linear piezoelectric effect leads to predictions in some cases opposite to those obtained using the widely used linear model.

Introduction

The piezoelectric (PZ) effect in III-V and II-VI semiconductors arises from lack of inversion symmetry along particular crystallographic directions [1,2]. It is generally regarded as a important factor in designing devices as diverse as light-emitting diodes (LEDs), lasers, power electronics, transducers and micropositioners. The recent discovery of the applicability of ZnO nanowires as mechanical energy sensors has originated a new field, Piezotronics [3–7]. The proposition of combining piezoelectric and electronic properties using semiconductor materials has great potential for the realization of self-powering devices, nanogenerators and flexible electronics.

In II–VI semiconductors, strain with a component along the polar axis of the crystal leads to the generation of electrical dipoles. In a wurtzite crystal such dipoles are linked to the diagonal strain tensor components and the resulting piezoelectric field is along the polar axis [0001]. Though the piezoelectric field in semiconductors has for a long time been treated as linear effect in the strain, the influence of non-linear components has been highlighted in zincblende II-VI [8], zincblende III–V [9–11] and wurtzite III-N [12,13] semiconductors.

In this paper we report the quadratic piezoelectric coefficients (PZCs) of ZnO and show that the magnitude of the coefficients is such that cannot be omitted in any calculation of the polarization field.

Methodology

The method, previously tested on III-As [9,10] and III-N semiconductors [12], comprises a semiempirical approach with piezoelectric charges given by the sum of a direct dipole contribution and a bond contribution, as originally proposed by Harrison [14].

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The linear and non-linear coefficients are determined through the total polarization, which is the sum of both spontaneous and strain induced polarization:

$$P_{\hat{x}_i} = \frac{Z_H^* \delta r + 2\alpha_p(1-\alpha_p^2)\cdot\sum_{q=1}^{4}(\rightarrow r_q \cdot \hat{x}_i)\delta R_q}{2\Omega} \quad (1)$$

where $\hat{x}_i$ is the Cartesian direction, δr is the displacement vector of cations in respect of anions from the ideal position, r_q and δR_q are the distance and displacement vectors of the nearest neighbor q from the atom at the centre of the tetrahedron, respectively, α_p is the bond polarity and Ω is the atomic volume. Borrowing from the language of tight binding, Z_H^* is the atomic charge, not to be confused with the dynamic effective charge or Born charge (Z^*), which is needed for evaluating the bond polarity:

$$Z^* = -\Delta Z + 4\alpha_p + 4\alpha_p(1-\alpha_p^2) \text{ with } \Delta Z = 2 \quad (2)$$

The atomic charge Z_H^* in our model is always determined so that, once α_p and the elastic deformation have been calculated in the limit of small strain (Bulk crystals), the model correctly reproduces experimental values of the PZCs.

For both bulk and strained cases, the elastic deformation and Z* were evaluated by using planewave pseudopotential (with pseudopotentials derived with the Troullier-Martin scheme [15]) density functional theory in the local density approximation (DFT-LDA) [16] and density functional perturbation theory (DFPT) within the CASTEP [17] code.

The dynamic effective charge was computed from the Born charge matrix, studied via the Berry phase approach [18] by applying a finite electric field perturbation in periodic boundary conditions. The matrix was then diagonalized and an average of the eigenvalues was taken as the effective charge. Both its bulk and strain dependence were determined in the same way.

DFT calculated equilibrium values are presented in Table 1 for ZnO together with the values of Z*, the resulting bond polarity α_p and the values of Z_H^*, which are much smaller than those of Z*, as explained earlier.

Table 1 Calculated and measured physical parameters for ZnO used in the calculations. Comparisons between our calculated values and other calculated and/or experimental ones are given in brackets.

Parameters	
a (Å)	3.18 (3.25 [21])$_{th}$
c (Å)	5.16 (5.207 [21])$_{th}$
u	0.375 (0.375 [21])$_{th}$
Z^*	2.164 (2.11 [21])$_{th}$
α_p	0.67 (0.69 [23])$_{th}$
Z_H^*	0.23
C_{33} (GPa)	176 [24]
C_{13} (GPa)	84 [24]
P_{sp}(C/m^2)	−0.01 (−0.057 [21], −0.047 [22])$_{th.}$
e_{33} (C/m^2)	1.15(1.22 ±0.04 [19], 0.96 [20])$_{exp}$
e_{31} (C/m^2)	−0.61(−0.51±0.04 [19], −0.62 [20])$_{exp}$
e_{311} (C/m^2)	3.98
e_{333} (C/m^2)	−5.59
e_{313} (C/m^2)	1.21

Piezoelectric coefficients

The ab initio DFT data is easily combined using Eq. (1), with the only difficulty being the calculation of the geometrical factor that multiplies the bond polarity. This requires combining the strained positions of all the atoms in the tetrahedron under consideration, which have already been obtained in the calculations of the internal distortion.

The result is the values of the total polarization for a given combination of a parallel and perpendicular strain. In order to obtain the linear and quadratic parameters e_{33}, e_{31}, e_{333} and e_{133}, the data is then fitted to the following equation:

$$P_{Tot} = P_{sp} + e_{33}\varepsilon_{\perp} + 2e_{31}\varepsilon_{||} + e_{311}\varepsilon_{||}^2 + e_{333}\varepsilon_{\perp}^2 + e_{313}\varepsilon_{||}\varepsilon_{\perp} \quad (3)$$

Since we need at least one of the linear parameters to obtain the correct value of Z_H^*, in this calculation, of the linear coefficients only e_{33} was fitted. For the coefficient e_{31} we had to make a suitable choice based on experimental values [19,20]. In choosing the value of e_{31} we ensured that the resulting calculated value of e_{33} would also be in the range of the available experimental data [19,20]. The values obtained are listed in Table 1. Note that in our model smaller values of the spontaneous polarization are predicted compared to previous calculations [21,22]. This is an expected result and the reason behind it is explained in detail in our previous work on wurtzite III-N semiconductors [12].

The dependence of the total polarization on strain in the range −0.08 to +0.08 according to the classic linear model (LM) and our non-linear (quadratic) model (NLM) is shown in Fig. 1. The main feature is that the NLM appear to always predict either less negative or more positive values of the polarization compared to the LM. This is part a result of the smaller values of the spontaneous polarization but also due to non-linear effects which manifest through the coefficients e_{333} and e_{133} when the strain is sufficiently large. We also notice that in some cases the LM and NLM predict opposite signs for the polarization, e.g. around 2% compressive parallel strain and no perpendicular strain gives a value of the total polarization of −0.04 C/m^2 or +0.01 C/m^2 using the LM or NLM respectively.

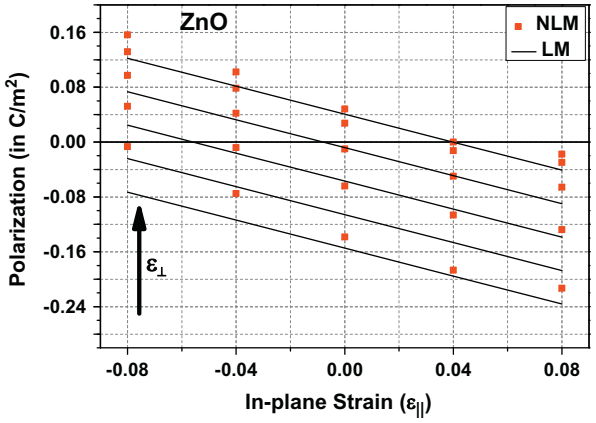

Fig. 1 Dependence of the total polarization (C/m^2) on strain in the range −0.08 to +0.08 according to the classic linear model (LM) and our non-linear (quadratic) model (NLM).

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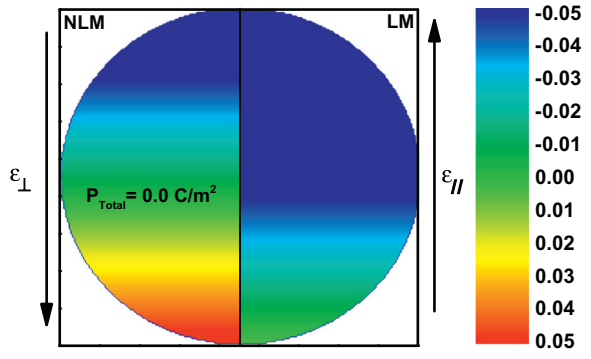

Fig. 2 Variation of the polarization (C/m^2) in a cross section of a ZnO nanowire. The perpendicular (parallel) strain varies from −2.8% (+2.8%) to +2.8% (−2.8%). The calculated polarization of the non-linear (quadratic) model (NLM) is on the left half and the classic linear model (LM) on the right.

The example of nanowires

We tested the LM and NLM by calculating the polarization in a ZnO nanowire subjected to a bending force deforming the cylindrical shape into an arch. For simplicity we assumed that such deformation would result in a polarization that is isotropic for each circular cross section of the nanowire. We also assume that the resulting perpendicular strain ε is antisymmetric along the section of the bent cylinder. Since in most materials compressibility is always lower than the ability to withstand tensile deformation, this is a correct assumption only for small strains. The perpendicular strain is related to the parallel strain $\varepsilon_{||}$ through the elastic constants of the material, given in Table 1:

$$\varepsilon_{\perp} = -\frac{2C_{13}(P)}{C_{33}(P)}\varepsilon_{||} \tag{4}$$

The combination of parallel and perpendicular strain is then used in Eq. (3) to evaluate the polarization.

In Fig. 2 we show the variation of the polarization for the case where the perpendicular (parallel) strain $\varepsilon_{\perp}(\varepsilon_{||})$ varies from −2.8% (+2.8%) to +2.8% (−2.8%). There are marked differences between the predictions of the LM and NLM. In particular the NLM predicts a gradient of the polarization ranging from −0.08 C/m^2 at the compressed end of the section, to +0.06 C/m^{2}at the tensile end. The LM polarization instead ranges from −0.12 C/m^2 to 0 C/m^2 within the same range of strains.

This demonstrates how the LM and NLM can produce opposite predictions.

Conclusions

We have estimated the linear and quadratic piezoelectric coefficients of ZnO wurtzite crystals. The magnitude of the quadratic terms is significant and necessitates inclusion even in the limit of small strain.

We showed calculations of the total polarization in ZnO nanowires and report that for particular strains originating from an external force the non-linear model of piezoelectricity predicts both positive and negative polarizations in the nanostructure whereas the linear model only predicts negative values.

Referenecs

[1] R.M. Martin, Physical Review B 5 (1972) 1607.
[2] W.G. Cady, Piezoelectricity, McGraw-Hill, New York, 1946.
[3] Z.L. Wang, Nano-piezotronics, Advanced Materials 19 (2007) 889–992.
[4] R.S. Yang, Y. Qin, L.M. Dai, Z.L. Wang, Nature Nanotechnology 4 (2009) 34–39.
[5] S. Xu, Y. Qin, C. Xu, Y.G. Wei, R.S. Yang, Z.L. Wang, Nature Nanotechnology 5 (2010) 366.
[6] Z.L. Wang, Scientific American 298 (2008) 82–87.
[7] R. Araneo, G. Lovat, P. Burghignoli, C. Falconi, Advanced Materials 24 (2012) 4719–4724.
[8] L.C. Lew Yan Voon, M. Willatzen, Journal of Applied Physics 109 (2011) 031101.
[9] M.A. Migliorato, D. Powell, A.G. Cullis, T. Hammerschmidt, G.P. Srivastava, Physical Review B 74 (2006) 245332.
[10] G. Bester, X. Wu, D. Vanderbilt, A. Zunger, Physical Review Letters 96 (2006) 187602.
[11] R. Garg, A. Hüe, V. Haxha, M.A. Migliorato, T. Hammerschmidt, G.P. Srivastava, Applied Physics Letters 95 (2009) 041912.
[12] J. Pal, G. Tse, V. Haxha, M.A. Migliorato, S. Tomic, Physical Review B 84 (2011) 085211.
[13] L. Pedesseau, C. Katan, J. Even, Applied Physics Letters 100 (2012) 031903.
[14] W.A. Harrison, Electronic Structure and Properties of Solids, Dover Publications Inc., New York, 1989.
[15] N. Troullier, J.L. Martins, Physical Review B 43 (1991) 1993.
[16] J.P. Perdew, A. Zunger, Physical Review B 23 (1981) 5048.
[17] S.J. Clark, M.D. Segall, C.J. Pickard, P.J. Hasnip, M.J. Probert, K. Refson, M.C. Payne, Zeitschrift für Kristallographie 220 (5-6) (2005) 567–570.
[18] M.V. Barry, Proceedings of the Royal Society of London A 392 (1984) 45.
[19] G. Carlotti, G. Socino, A. Petri, E. Verona, Applied Physics Letters 51 (1987) 1889.
[20] I.B. Kobiakov, Solid State Communications 35 (1980) 305.
[21] F. Bernardini, V. Fiorentini, D. Vanderbilt, Physical Review B 56 (1997) R10024.
[22] S. Massidda, R. Resta, M. Posternak, A. Baldereschi, Physical Review B 52 (1995) (R)16977.
[23] W.A. Harrison, Physical Review B 10 (1974) 767.
[24] S.-H Hang, S.F. Chichibu, Applied Physics Letters 112 (2012) 073503.

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