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Nonlinear piezoelectricity in wurtzite semiconductors

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We present first-principles calculations of piezoelectric coefficients of first and second order for AlN, GaN, InN, and ZnO, along with the composition dependence (bowing) of the linear terms. We show that eight second order coefficients are required and provide a simple description on how to incorporate second order effects in the calculation of the polarization and fields. We demonstrate that the second order effect leads to corrections of the order of 15% for quantum wells and up to 40% for epitaxial quantum dots.

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Noncentrosymmetric materials exhibit piezoelectric behavior of very different magnitude. Nitrides and ZnO in the wurtzite structure exhibit a large spontaneous and piezoelectric polarization that can lead to fields in the megavolt/cm range.[1] Many optoelectronic devices, such as light emitting diodes, photovoltaic cells, or even the stability of quantum bits in nanostructures depend on these fields. In some cases, the field itself gives the device its functionality like in surface acoustic wave resonators, in filters, in sensors, and in micromechanical systems. Quantum wells (QWs) and quantum dots (QDs) made of nitride or ZnO can be under extreme strain conditions[2–9] and consequently, the linearity of the piezoelectric effect on the strain can be questioned. For instance the second order effect has been demonstrated to be important for zincblende III-V semiconductors[10,11] and, in III-nitride wurtzite materials, Ambacher *et al.* have shown some nonlinearities in the piezoelectric effect for the particular (0001) interface.[12]

In this Rapid Communication we establish the theoretical framework in which the second order piezoelectric tensor can be simplified in the wurtzite symmetry and how it can be calculated *ab initio*. We determine the three first and the eight second order piezoelectric coefficients for Al(Ga,In)N and ZnO. The latter are found to be up to 30 times larger than the linear coefficients. The second order coefficients play a significant role for high values of the strain. Furthermore, we estimate the nonlinearity in the piezoelectric coefficients with respect to the ternary composition and find a large bowing for In based compounds. The piezoelectric polarization is defined for arbitrary growth directions and a qualitative difference appears when second order terms are included. Finally the piezoelectric field is calculated for several nanostructures and found to be in good agreement with available experimental data. The nonlinear terms modify the field by about 15% in QWs and by about 40% in QDs.

The piezoelectric polarization P_μ as a function of mechanical strain η_j (in Voigt notation) can be written up to the second order in strain as[10]

$$P_\mu = \sum_{j=1}^{6} e_{\mu j}\eta_j + \frac{1}{2}\sum_{jk=1}^{6} B_{\mu jk}\eta_j\eta_k, \qquad (1)$$

where $e_{\mu j}$ is the proper piezoelectric tensor of the unstrained material and $B_{\mu jk}$ represents the first-order change of the piezoelectric tensor with strain. Among the 18 possible linear coefficients $e_{\mu j}$, five are nonzero with three being independent:

$$e_{33}; \quad e_{31} = e_{32}; \quad e_{15} = e_{24}. \qquad (2)$$

In order to calculate the second order bulk piezoelectric coefficients, a finite difference technique has been used in combination with density functional perturbation theory (DFPT) within the local density approximation (LDA). The calculations were done with the Abinit Package[13,15] using the Troullier-Martins (TM) pseudopotentials[14] prepared by the Fritz Haber Institute code. The numerical results were computed by treating the electrons of the 3d (Ga, Zn) and 4d (In) level as valence states. Plane waves up to 90 Ha (for ZnO, 70 Ha for the others) were used to expand the electronic states and the Brillouin zone was sampled with a 8 8 6 k-points mesh for the piezoelectric and elastic coefficients and a 12 12 8 k-points mesh for the dielectric coefficients. Details of our methodology have been described elsewhere.[10,11]

To reduce the number of coefficients we start with the 243 (3^5) coefficients of the fifth rank tensor $B_{\mu\alpha\beta\gamma\lambda}$ (in cartesian coordinates) and use the symmetry operations of the point group. We identify the possible combinations of $(\mu\alpha\beta\gamma\lambda)$ that leave the tensor $B_{\mu\alpha\beta\gamma\lambda}$ unchanged under the transformation $B_{\mu\alpha\beta\gamma\lambda} = a_{\mu p}a_{\alpha q}a_{\beta r}a_{\gamma s}a_{\lambda t}B_{pqrst}$ where a_{ij} is a matrix representation of one of the symmetry operations. In Voigt notation the possible 36 combinations of jk can be reduced to 21 since $B_{\mu jk} = B_{\mu kj}$. Finally we have 17 nonzero coefficients with 8 being independent. The form of the second order piezoelectric tensor for the wurtzite point group is given in Table I in a form adapted from Nelson[16] and Grimmer.[17] The rows give the index μ and the columns both Voigt index jk.

The redundancy in Table I allows us to calculate the coefficients using different types of deformations and cross check their accuracy. We have furthermore calculated the B_{333} coefficients using the Berry phase approach[18] and found very good agreement (less than 3% deviation) with the value determined from DFPT. In our previous work[11] we have shown that a straightforward calculation leads to improper second order piezoelectric coefficients (analogous to the improper linear coefficients[19]) that need to be corrected in order to obtain the meaningful proper coefficients.

The piezoelectric coefficients are given in Table II showing that the second order coefficients are typically one order of magnitude larger than the linear ones. B_{333}, which governs the second order polarization under strain along the c axis, is the

TABLE I. Form of the second order piezoelectric coefficients $B_{\mu jk}$ for the hexagonal wurtzite point group (6mm). There are eight independent coefficients a-h. The symbol · indicates vanishing coefficients. The rows (columns) corresponds to the index μ (jk) in $B_{\mu jk}$.

	11	22	33	44	55	66	12	13	23	45	36	26	16	25	15	35	46	14	24	34	56
1	·	·	·	·	·	·	·	·	·	·	·	·	·	$2b$	$2a$	c	a-b	·	·	·	·
2	·	·	·	·	·	·	·	·	·	·	·	·	·	·	·	·	·	$2b$	$2a$	c	a-b
3	$2d$	$2d$	g	h	h	d-e	$2e$	f	f	·	·	·	·	·	·	·	·	·	·	·	·

largest coefficient for all the materials investigated and can induce significant second order effects especially in material with a rather small linear coefficient e_{33}. The case of GaN is noteworthy as it may explain the experimental overestimation of e_{33} at 1.12 C/m^2.[20]

The experimental nitride structures being mainly made of ternary alloys, we have studied the nonlinear dependence of the piezoelectric tensor on the composition of these alloys by constructing $A_{0.5}B_{0.5}N$ simulation cells and by calculating the bowing coefficients b^{ABN} defined by the following quadratic relation:

$$e_{\mu j}^{A_x B_{1-x} N} = x e_{\mu j}^{AN} + (1-x) e_{\mu j}^{BN} + x(1-x) b_{\mu j}^{ABN}. \quad (3)$$

The bowing coefficients are given in Table III along with the relative lattice mismatch $\Delta a/\langle a\rangle$ and the relative piezoelectric coefficient difference $\Delta e_{33}/e_{33}$ between the binaries. For each material, the b_{33} coefficient is larger than b_{15} and b_{31}. It is interesting to notice that neither the lattice mismatch nor the piezoelectric coefficient difference give a clear trend related to the bowing coefficient.

Then the piezoelectric polarization is calculated from Eq. (1) for an arbitrary crystallographic direction by assuming pseudomorphic growth and by using the elastic coefficients of the materials to obtain the full strain tensor. The results for InN/GaN (where GaN represents the substrate) are given in Fig. 1 as polar plots for the magnitude of the polarization (top) and for the electric field (bottom) using only the linear piezoelectric coefficients (left) and using linear and second order coefficients (right). The electric field is calculated using the relation $E = -\frac{P}{\varepsilon_w \varepsilon_0}$ where P is the projection of the polarization vector along the growth direction, and ε_w and ε_0 are the static dielectric constants of the barrier and vacuum, respectively. For this extreme case (InN and GaN have a large lattice mismatch), that may be given in QDs,[5–7] the inclusion of the second order effect changes the results for the polarization qualitatively. It changes from a nearly ellipsoidal shape to a more complex shape with maxima along the $\{1\bar{1}02\}$ directions. Especially the polarization along the [0001] direction is reduced by nearly a factor of two due to the second order terms.

Most experiments deal with superlattices or QWs grown along the [0001] direction which is also the direction of the spontaneous polarization P_{sp}. Our P_{sp} values are reported in Table II and are found to be in good agreement with previous calculations[1,12] and with a recent experiment for GaN (-0.022 ± 0.005 C/m^2).[21] For pseudomorphic growth along the [0001] direction the strain tensor simplifies significantly to $\eta_1 = \eta_2 \neq \eta_3$, $\eta_4 = \eta_5 = \eta_6 = 0$. The components of the strain tensor are related through the Poisson ratio ν (under the assumption $\sigma_3 = 0$):

$$\eta_3 = -2\frac{C_{13}}{C_{33}}\eta_1 = \nu\eta_1 = \nu\frac{a-a_0}{a_0}. \quad (4)$$

The piezoelectric polarization pointing along the [0001] direction is given by

$$\begin{aligned} P_3^{pz} &= (2e_{31} + e_{33}\nu)\eta_1 \\ &\quad + \frac{1}{2}(2B_{311} + 2B_{312} + B_{333}\nu^2 + 4B_{313}\nu)\eta_1^2 \\ &= (2e_{31} + e_{33}\nu)\eta_1 + (2d + 2e + \frac{g}{2}\nu^2 + 2f\nu)\eta_1^2. \end{aligned} \quad (5)$$

and is displayed in Fig. 2. We plot the polarizations due to the linear terms only (dotted lines), the linear + bowing effects (dashed lines), and the linear + bowing + second order effects (solid lines), for each of the ternary compounds on each possible substrate. Note that the polarization with only linear terms (dotted lines) is already nonlinear because of the composition dependence of the elastic and lattice constants that are calculated according to Vegard's law. The polarization is highly affected by second order contributions for In rich QWs (like InN/AlN, GaN/InN, and InN/GaN) while the other materials show only weak second order effects. GaN/AlN and AlN/GaN particularly show a very small piezoelectric effect due to the small lattice mismatch. In the intermediate composition range ($x \simeq 0.5$) the bowing of the piezoelectric coefficients is apparent. In general, when the second order coefficients are important (solid line deviating from the dashed line), the magnitude of the polarization is reduced.

TABLE II. Piezoelectric coefficients and spontaneous polarization P_{sp} in (C/m^2). We assign error bars for the values obtained for InN due to the poor description of this material within the LDA.

	$2a$	$2b$	c	$2d$	$2e$	f	g	h	e_{15}	e_{31}	e_{33}	P_{sp}
AlN	4.4	2.4	−0.1	3.0	3.0	3.8	−26.0	3.2	−0.35	−0.67	1.67	−0.095
GaN	3.8	2.3	2.7	6.2	3.3	0.4	−21.4	0.4	−0.31	−0.44	0.75	−0.027
InN	4.5[±0.4]	2.8[±0.2]	1.6[±0.4]	4.8	3.7	0.5[±0.1]	−18.6	0.5	−0.43	−0.59	1.14	−0.035
ZnO	3.0	2.5	1.4	3.5	3.7	0.0	−14.1	0.9	−0.53	−0.68	1.31	−0.042

TABLE III. Bowing coefficients (MV/cm^2) for the nonlinear dependence on ternary composition for the linear piezoelectric coefficients and lattice mismatch $\Delta a/\langle a\rangle$ (Å) and $\Delta e_{33}/\langle e_{33}\rangle$ piezoelectric coefficients difference (C/m^2) between binaries.

	b_{15}	b_{31}	b_{33}	$\Delta a/\langle a\rangle$	$\Delta e_{33}/\langle e_{33}\rangle$
GaN/AlN	−0.032	0.106	−0.671	2.23%	75%
GaN/InN	−0.275	0.222	−0.550	10.4%	41%
InN/AlN	−0.305	0.540	−2.178	12.65%	38%

Using the Berry phase approach[18] Ambacher *et al.*[12] fitted the piezoelectric polarization of binary group III nitrides by including a quadratic dependence on the strain. The calculated piezoelectricity for GaN was found to be $P_{\mathrm{GaN}} = -0.918\eta_1 + 9.541\eta_1^2$, similar to the relation derived from this work:

$$P_{\mathrm{GaN}} = -1.18\eta_1 + 7.38\eta_1^2.$$

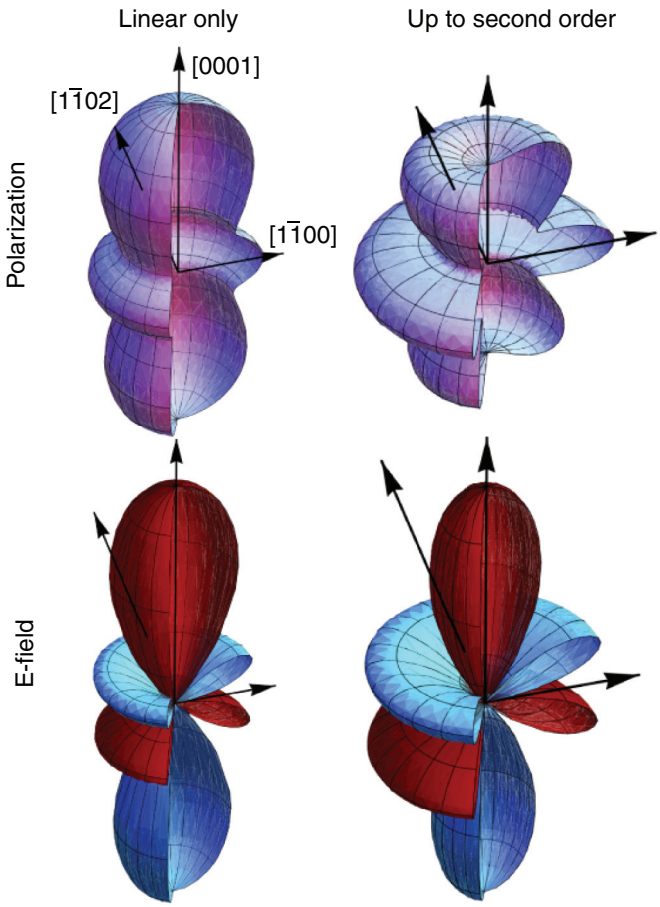

FIG. 1. (Color online) Spherical polar plots of the magnitude of the polarization (top) and of the piezoelectric field (bottom) in a pseudomorphic InN/GaN quantum well of arbitrary crystallographic orientation. The Euler angles θ and ϕ give the direction of the growth axis, and at the same time the orientation of the piezoelectric field. The blue and red colors for the field indicate if the field is oriented parallel or antiparallel to the growth direction, respectively. Numerical values along the [0001] direction: polarization (linear/nonlinear) 0.2669/0.1762 C/m^2; electric field (linear/nonlinear) −19699/−13008 kV/cm.

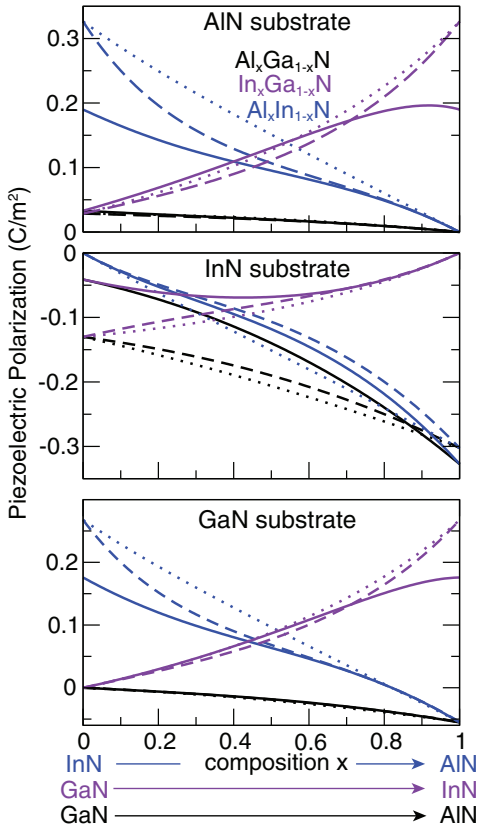

FIG. 2. (Color online) Piezoelectric polarization with respect to the ternary compositions for different compounds on different (0001) substrates. The curves are P_l^{pz} (dotted line), P_l^{pz} with bowing (dashed line), P_l^{pz} with bowing + P_{nl}^{pz} (full line).

For the other nitrides we obtain the following relations:

$$P_{\mathrm{AlN}} = -2.20\eta_1 - 1.32\eta_1^2$$
$$P_{\mathrm{InN}} = -2.70\eta_1 - 9.37\eta_1^2.$$

Recently,[22,23] second order piezoelectric coefficients were computed from Harrison's model. The results are, however, hardly comparable to available data because of the omission of the coefficient B_{312}, which is necessary for the polarization calculation, and because of the attribution of a finite value to B_{133}, which should be null by symmetry. The second order coefficients were also computed in Ref. 24 within the Berry Phase approach, but the authors admitted the use of an underconverged cutoff and the lack of the necessary corrections to "improper" coefficients (see Ref. 11). However this error should not affect the main conclusions of the authors concerning the electrostriction and the coupling effects on the electric field.

After calculating the polarization, we now compute the ensuing electric field in a quantum well, in the same way as in Ref. 11 and compare the results to available experimental data. Leroux *et al.*[25] emphasize that in their sample the strain does not develop in the GaN QW but rather in the alloy substrate. Since it is not obvious to guess which slab is strained, we have computed the field by considering either a strained well or a strained barrier, for barrier and well thinner than 6 nm. Experimental and theoretical results are reported in

TABLE IV. Electric field (MV/cm^2) as reported experimentally and from our theoretical calculation using our P_{sp}, linear and nonlinear piezo coefficients. l_w and l_B denote the thicknesses of the well and of the barrier, respectively.

QW/Barrier	E^{exp}	E_{theory}	l_w/l_B(nm)
		this work	
GaN/AlN	8.2–10.2 (Ref. 26)	10.2–10.4	2.6–0.7/100
GaN/AlN	8 (Ref. 27)	7.7–10.6	2.6/6.4–1.25/5
GaN/AlN	9.0–11.0 (Ref. 28)	5.9–10.3	0.8–2.5/2.8
GaN/$Al_{0.11}Ga_{0.89}N$	0.45 (Ref. 25)	0.4(5)–0.5(5)	2.3–3.9/5
GaN/$Al_{0.17}Ga_{0.83}N$	0.72–0.88 (Ref. 29)	1.2(5)	4/infinite
GaN/$Al_{0.65}Ga_{0.35}N$	2.0 (Ref. 30)	2.8(6)–4.2(5)	6-3/6
$In_{0.11}Ga_{0.89}N$/GaN	1.33	1.6(8)–1.7(7)	3-6/50

Table IV. The field is computed by using P_{sp}, linear, bowing, and second order piezoelectric coefficients. The relative agreement between the experimental values and the DFT is satisfying considering the uncertainty in the experimentally determined elastic constants we use in the calculation of the fields, and in the models used to extract the fields from the experimental raw data (see Ref. 11 for a discussion of these effects).

In summary, the second order piezoelectric effects are rather small for typical quantum wells where the achieved lattice mismatch does not exceed 1%. However in thin films or in quantum dots, where heavily strained structures can be obtained[3,4] the second order effects can be very significant and modify the fields by up to 40%. The composition dependence (bowing) of the piezoelectric coefficients for intermediate compositions is shown to affect the results in a range of 10 to 20%.

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