

Title	Strain effects in wurtzite BN: elastic constants, internal strain and deformation potentials from hybrid functional density functional theory
Authors	Sheerin, Thomas P.;Schulz, Stefan
Publication date	2022-03-18
Original Citation	Sheerin, T. P. and Schulz, S. (2022) 'Strain effects in wurtzite BN: elastic constants, internal strain and deformation potentials from hybrid functional density functional theory', Physica Status Solidi - Rapid Research Letters. doi: 10.1002/pssr.202200021
Type of publication	Article (peer-reviewed)
Link to publisher's version	10.1002/pssr.202200021
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Strain effects in wurtzite BN: elastic constants, internal strain and deformation potentials from hybrid functional density functional theory

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Keywor is: Wirtzite boron nitride, hybrid density functional theory, HSE functional, deformation potentials, elastic constants, internal strain parameters

Boromantaling III-nitride heterostructures have recently attracted significant attention for improving the efficiency of visible and UV light emitters. However, the fundamental material properties of *warrate* BN are largely unexplored. Here, highly accurate first principles calculations are used to gain integrit into internal strain, elastic constants and electronic band structure deformation toten als. These parameters are key ingredients for simulating, and thus predicting, electronic and optical properties of boron-containing III-nitride-based light emitters. The ab initio calculations show, for instance, that the quasi-cubic approximation for deformation potentials is a poor approximation for wurtzite BN.



Controlling, toiloring and engineering the crystal phase of semiconductor materials has received strong interest in recent years^[1, 2]. From the perspective of fundamental physics, crystal phase controllement ostructures are ideal candidates for demonstrating quantum effects (e.g. the Aharanov-Bohn effect of excitons^[1]). These all-binary quantum structures exhibit flat interfaces and the absence of allow fluctuations^[1]. In addition, changing the crystal phase of a material may allow for changing its fundamental properties. For instance, as demonstrated in Ref.^[2], while Ge is an indirect bandgap material man cubic (diamond) phase it becomes a *direct* gap material in the hexagonal (lonsdaleite) physe. This finding is highly attractive for silicon photonic device applications. Overall, to drive the uncerstanding of fundamental properties but also to design future devices, theoretical modelling is an essential ingredient. Here, density functional theory (DFT) plays an important role, since (i) it can frovid insight into the fundamental material properties from first principles and (ii) the insight obtain form the basis and input for developing empirical atomistic^[3, 4] but also continuum-based^[5, 6] models that allow for simulating full device structures.

Here we present results from highly accurate hybrid DFT studies on the properties of *wurtzite* (WZ) BN. While a N preferentially crystallizes in the hexagonal (2D) or zincblende phase^[7], it has recently drawn attention for alloying WZ III-nitride semiconductors InN, GaN and AlN^[8, 9, 10, 11, 12, 13]. Despite the fact that bulk WZ BN is difficult to synthesize, several works have succeeded in incorporating small fractions of WZ BN (mainly up to 10%, with some exceptions of slightly larger

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the <u>Version of Record</u>. Please cite this article as <u>doi: 10.1002/pssr.202200021</u>.

values near 20%) into other WZ III-nitrides^[8, 10, 12, 13]. Using WZ BN in III-N materials is thus attractive for optimizing the efficiency of e.g. light emitting diodes operating in the visible^[9, 8] to ultraviolet^[12, 11] spectral range. Recent theoretical studies on WZ BN have mainly focused on the band gap, piezoelectric coefficients and band offsets^[14, 15]. But, to perform full device simulations using, e.g., continuum-based $\mathbf{k} \cdot \mathbf{p}$ models, parameters such as band gap deformation potentials and elastic constants are required. We provide insight into these properties, along with internal strain parameters, which are essential for developing atomistic force-field models.



Figure 1: (Color online) The electronic band structure of wurtzite BN. The color-coding indicates the *s*- and *p*-orbital character of the different bands. Labels for selected states (K_c , Γ_c , $\Gamma_{1\nu}$, $\Gamma_{6\nu}$), important for deformation potential calculations, are also given.

transfers in this work are derived from highly accurate hybrid functional DFT All m calculations, using the projector-augmented wave method implemented in the plane-wave-based ab initio code VA: $P^{[16, -1]}$. The plane-wave cutoff is set at 600 eV and a Γ -centred 8.86 k initial mesh is used in all calculations. Here, we employ the Heyd-Scuseria-Ernzerhof (HSE) functional[18] with a screenin rameter of $\mu = 0.2$. To perform calculations for WZ BN, we use GaN as a starting first benchmark the outcome of our calculations with existing results for GaN point. In doing from the literature before predicting data for WZ BN. Thus, we use the HSE exchange-mixing parameter to let to be experimental bandgap of WZ GaN (3.51 eV^[19]); the resulting value ($\alpha = 0.284$, which is in good agreement with previous HSE-DFT studies^[20]) is then used for all WZ BN calculation, since the bandgap of WZ BN has not been conclusively determined experimentally. tained WZ BN band structure. Our calculations predict an indirect band gap of Figure 1 shows $E^{K} = E^{K_{c}}$ $\Gamma_{\rm c}$ (see discussion below) of eV and a transition energy to $= E^{\frac{1}{6}v}$ 0.09 eV, which are in good agreement with theoretical literature data^[15, 14]. E^{1}

Having considered the equilibrium electronic properties of WZ GaN and BN, we now proceed to obtain parameters that come into play when the crystal is strained. In this work, we focus on the deformation potentials a_c and D_p the elastic constants C_{ij} and the internal strain parameters ζ_i . We begin with the deformation potentials. These parameters are key ingredients when calculating the electronic and optical properties of semiconductor heterostructures in the frame of semi-empirical atomistic approaches (e.g. tight-binding^[3]) or continuum-based models (like k p theory^[5]). We note however that care must be taken when deriving deformation potentials from our DFT data, especially for use in k p models. Since the WZ III-nitrides InN, GaN and AlN are *direct* gap

Defo. Pot.	GaN	GaN		BN	
[eV]					
	Present	Lit.	Present	Lit	
$a_{cz} - D_1$	-6.03	-5.81	-2.36	_	
$a_{ct} - D_2$	-8.98	-8.92	-24.44	_	
D 3	5.38	5.47	2.71	3.90	
	-2.95	-2.98	-2.74	-3.32	
	-2.80	-2.82	-4.05	-4.30	
	-3.95	-3.95	-6.42	—	
ADPs 🟉			L		
a _{cz}	-8.60	-	-3.33	_	
a _{ct}	-6.22	_	-21.42	_	
	-2.56	-20.0	-0.97	-19.2	
D 2	2.76	-14.2	3.02	-14.0	

nd GaN deformation potentials obtained are summarized in Table 1. The GaN data show very good agreement with previously published HSE-DFT data, lending trust that the chosen approach should also provide highly accurate results for WZ BN. There exist no HSE-DFT literature data yas the deformation potentials of BN and even for DFT within the local density approximation LDA DFT) the data are sparse (see e.g. Ref.^[26]); the inaccuracies of LDA-DFT in predicting electronic properties are well known and thus our HSE-DFT provides more accurate data, as well as data ha were not available before (e.g. $D_{\sigma}a_{ce} - D_{1}$ and $a_{ci} - D_{2}$). Overall, when comparing GaN and BN data, while most of the deformation potentials are similar in terms of sign D_{2} , is almost a factor of 3 larger in BN. Such a large deformation potential can and magnitude, strongly affect the band edges in a heterostructure and thus the carrier confinement. However, the present approace doe not allow us to distinguish if this will affect the conduction (a) or valence ($a_{ct} - D_{2}$. Determining the *absolute* D) band more strangly, since we only have access to deformation poen ial (ADPs) from DFT is challenging. To gain first insight into the ADPs, we use the 1s core level as the reference point for our energy scale and assume this level is independent of the applied stran. A detailed critical discussion of this approach can be found in Ref.^[27], but since we are aiming for final sights into the ADPs, this approach should be sufficient for our purposes.

The ADPs obtained for WZ BN and GaN are given in Table 1, along with literature data for comparison. Our values for the ADPs differ from those of Ref^[26], e.g. we get different signs for D_{2} . However, Ref.[26] uses not give information about the reference energy. It seems that the energy scale set by the electronic structure calculation is used- this is, however, not absolute. Thus, our results should give more accurate first insight into the ADPs. We briefly note that for both $a_{cz} = D_{1}$ and $a_{ct} = D_{2}$ in BN, the CB accounts for most of the movement under strain.

In a further step, we study the validity of the quasi-cubic approximation (QCA), which is often applied[28, 21] in studies of WZ III-N systems because not all deformation potentials may be known accurately from experiment or theory. The QCA results, for instance, in $D_3 + 2D_4 = 0$ and $D_3 + 4D_5 - \sqrt{2}D_6 = 0$. Using our calculated values, for GaN we find a value of -0.52 eV for $D_3 + 2D_4$, which is consistent with Ref.^[25]; for WZ BN this value is -2.77 eV, deviating significantly

from zero. Looking at $D_3 + 4D_5 - \sqrt{2}D_8$ which again should be zero, for GaN we obtain -0.23 eV but for BN it is -4.41 eV. All this shows that the QCA is a very poor approximation for WZ BN and highlights the importance of our highly accurate first-principles calculations. It is interesting to consider why WZ BN violates the QCA to a far greater extent than WZ GaN. We partly attribute this, as in Ref.^[29], to deviations of BN from the ideal WZ structure. However, these deviations are slight, and GaN suffers similar deviations from ideality: the *u*-parameter of BN is, from Table 2, equal to the ideal of 0.375, but its c/a ratio is noticeably larger than the ideal $\sqrt{8/3}$ value; the reverse is true for GaN. As discussed in Ref.[29], further contributions to the breakdown of the QCA in WZ materials may ars from (strong) 3rd nearest-neighbor interactions. Indeed, the lattice constants of BN are $\sim 20\%$ for er than those of GaN, and as a consequence one could expect stronger 3rd nearest-neighbor interactions in WZ BN than in WZ GaN, since the atoms are closer to each other.

To calculate plastic properties, we use the stress-strain method, since in general this leads to a faster and smoother convergence with respect to k-point sampling and cutoff energy[30]. Choosing such an approach is particularly beneficial for the numerically demanding HSE-DFT framework used here. To determine the elastic constants C_{ij} we employ the stress-strain relation:

$$\sigma_{i} = \sum_{i} C^{\varepsilon}_{ijj}, \qquad (2)$$

where σ_{ij} is the *j* th stress-tensor component and ε_{ij} the *j* th strain-tensor component (Voigt notation). Subjecting the lattice to each of the four strain branches used for the deformation potentials above and extracting the strain tensor from VASP allows determination of the C_{ij} by fitting (again over the $\pm 2\%$ strain range).

Table 2: Independent elastic tensor components C_{ij} and bulk modulus *B* of WZ GaN and BN, along with lattice constants and *u*-parameter, as predicted by this work ("Present"). WZ BN literature ("Lit.) cata have been taken from Refs.^[26, 15, 31], while for GaN data from Refs.^[32, 19, 30] are

		GaN		BN	
			Lit.		Lit.
	Ì			Present	
	C	377	390	1016	982
[GPa]					
	C 12	137	145	144	134
[GPa]					
	C 13	92	106	64	74
[GPa]					
	C 33	407	398	1113	1077
[GPa]					
	C 44	103	105	361	388
[GPa]					
	В	200	210	410	401
[GPa]					
	a [Å]	3.174	3.189	2.534	2.549
	c [Å]	5.165	5.185	4.189	4.223
	и	0.377	0.377	0.375	0.374

given.

Table 1 summarizes our calculated elastic constants, including the bulk modulus B, for WZ GaN and BN. We also display the lattice constants and the *u*-parameter, and compare all data to the literature. Overall, for GaN we find very good agreement with the literature^[32]. For WZ BN, the agreement with the literature is also good. However, for C_{p_1} , C_{12} , and C_{33} our values are larger while C_{13} is lower compared to Ref.^[26], which uses LDA-DFT. It has already been discussed in the literature that HSE-DFT is in general superior to LDA calculations for predicting structural properties^[33]. Thus, our results are expected to be more accurate. Comparing the results for GaN and BN, we note that the diagonal components C_{μ} of the elastic tensor are a factor of order 3 larger in WZ BN. This is an important observation for c -plane WZ quantum wells (QWs), the "standard" ed optoelectronic devices. In such a system, the strain along the *c* -axis can be structure for III approximated by $\epsilon = -2(C_{13} / C_{33})$, where ϵ_1 is the strain in the growth (c) plane given by $e_1 = (a_B - a_W)/a_W$, where a_W (a_B) is the well (barrier) in-plane lattice constant. Thus, given the much larger value of C_{13} and smaller value of C_{13} in BN when compared to GaN, the ratio C_{11}/C_{13} should reduce when adding BN to a GaN QW. Also, when considering a BGaN QW grown on AlN, the singler fattice mismatch results in a reduction of ε_1 This means that the overall strain in such a system will be smaller compared to GaN/AlN, in turn causing a reduction in the piezoelectric polarization field 341 this should be highly beneficial for the radiative recombination rate in BGaN/AIN QU's. Iowever, further studies are required to gain insight into this question.

Finally, the etermine the internal strain parameters we proceed largely as described in Ref.^[30]. Starting from the unstrained atomic positions of the two anions and cations in the WZ unit cell (see Figure 2), we apply strain to the lattice so that the positions become^[30]

$$\begin{array}{c} \left(\begin{array}{c} \bullet \\ \bullet \end{array} \right) \mathbf{r}_{0}^{B} + \mathbf{t}_{p} \\ \left(\begin{array}{c} \bullet \\ \bullet \end{array} \right) \mathbf{r}_{0}^{C} + \mathbf{t}_{2} \\ \left(\begin{array}{c} \bullet \\ \bullet \end{array} \right) \mathbf{r}_{0}^{D} + \mathbf{t}_{3} \end{array} \right)$$
(3)

where \mathbf{r}_{0}^{A} , \mathbf{r}_{0}^{C} , \mathbf{r}_{0}^{D} and \mathbf{r}_{0}^{D} denote the unstrained atomic positions, is the 3 × 3 identity, ε the strain tensor and \mathbf{t}_{i}^{D} be internal strain displacement vectors. Since we use different coordinates to Ref.^[30], each t_{i}^{D} be the basis transformed strain tensor. Since we use different coordinates to Ref.^[30], each t_{i}^{D} be the basis transformed strain tensor. $f_{i}^{D} = \mathbf{R}_{i}^{D} \mathbf{r}_{i}^{D}$

We obtain the internal strain parameters ζ_i (i = 1 - 5) by applying the four strain branches from before and fitting to be above expressions.



Figure 2: (Color online) The unit cell used in this study for the WZ crystal structure. Red (blue) denotes actions (anions), and stripe-filled circles belong to adjacent unit cells.

In all our calculations we constrain the internal displacements of the ions in the unit cell to conform to the symmetry of the WZ crystal, similar to Ref.[30]. This minimizes the impact of any numerical error that this symmetry-constraining has almost no effect on the deformation potentials and elastic constants, but is important for ζ_1, ζ_2 and ζ_{s} . The integral strain parameters obtained are shown in Table 3. For GaN we find very good agreement with previously published results, except for ζ_{1} . In general, since ζ_{4} and are determined from strain branches that break the original C_{6v} WZ symmetry to smaller groups, they are quite sensitive to fine details of the calculation, like whether or not one uses the "symmetry tined above. Presumably, we and Ref.[30] use somewhat different settings in our constraining" m calculations, which are explain the deviations in ζ_{1} . The exact origin of the sensitivity in ζ_{1} and nt to ic but beyond the scope of this work. A comparison with the literature is not ζ_{ζ} is an import possible for WZ BJ since there are no previously published data. An accurate theoretical determination of the internal strain parameters is important for three reasons. Firstly, it is experimentally not possible to determine these parameters with approaches currently available. parameters ζ_i provide input to, but also a way to benchmark semi-empirical Secondly, interr an[6]. Thirdly, internal strain parameters are tightly linked to local polarization interatomic pot r at rials, which in turn can lead to strong carrier localization effects[3, 35]. effects in III-N Comparing WZ GaN and BN, we find that the internal strain parameters ζ_{j} are much smaller in BN. This means the shift if the atomic positions is mainly determined by the macroscopic strain, so local piezoelectric effec and contributions to carrier localization effects may be reduced.

Table	3: The timensionless) internal strain parameters	ζ_{i} of WZ GaN and BN ("Present"), æ
	presented in this work. GaN literature data a	are also given ^[30] ("Lit.").

Ś,	GaN		BN
	Present	Lit.	Present
ζ_{1}	0.155	0.156	0.051
ζ	0.082	0.083	0.015
ζ 3	0.156	0.159	0.007
ζ 4	0.199	0.201	0.049
ζ 5	0.097	0.141	0.051

3 Conclusion

In summary, by using highly accurate first principles calculations, we provide insight into internal strain, elastic constants and electronic band structure deformation potentials of WZ BN. This material has attracted significant attention as a potential candidate to improve the efficiency of III-N-based devices. The parameters determined are key ingredients for simulating, and thus predicting, electronic and optical properties of boron-containing III-N light emitters. Our calculations show, for instance and the QCA for deformation potentials is a poor approximation for WZ BN, highlighting the model of our accurate DFT study.

Acknowledgements

This work re-eived funding from the Sustainable Energy Authority of Ireland and the Science Foundation Ireland (Nos. 17/CDA/4789 and 12/RC/2276 P2).

Confinet of Interest

The authors declare no conflict of interest.

Data Andilability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.



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Table of Contents text

The deformation potentials, elastic constants and internal strain parameters of wurtzite (WZ) BN are determined using hybrid density functional theory. WZ BN is a promising material for optimizing the efficiency of III-nitride-based devices, and these parameters are essential input for modelling of such systems. The results also show e.g. that the quasi-cubic approximation is very inaccurate for WZ BN.

