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Reconsideration of Deformation Potential Constants in Nitride Semiconductors with Wurtzite Structure

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Abstract. The deformation potential in nitride semiconductors with wurtzite structure is theoretically re-examined. The ligand field potential term including the trigonal part is definitely dealt in the model. The alternative approach to the expression for the deformation potential constants is tried in the framework of invariant regime. The basic expressions derived by perturbation theory are given, where the deformation potential constants are defined for the stresses instead of the strains, because this definition is much more straightforward for experimentalist.

1. Introduction
Examining the responsiveness of materials to external perturbations such as electric, magnetic fields and stress, it is often required in device design. In multi-quantum well systems of semiconductors, the interfacial stresses are inevitably generated, affecting the various physical properties of the semiconductors such as the band gap. The effects are especially pronounced in semiconductors with a wurtzite structure because three valence band states lie in close proximity.

The effects of strain on the band structures of semiconductor have been under investigation for half a century. Bir and Pikus [1] developed a general expression for these effects in semiconductors including those with wurtzite structure, which belongs to the space group P63mc. Their energy matrix is widely used in a variety of situations, and they defined six deformation potential constant (DPC) s in wurtzite crystals, two (Dc1 and Dc2) for the conduction band and four (D1 D2, D3 and D4) for the valence band. For a hexagonal GaN under the stresses, the ligand field splitting parameter Δ1 may play a particular role on the alignment of three valence band states because the spin-orbit and the ligand field splitting energies are both small (< 20 meV) [2], leading to an easy rearrangement of the three valence bands under stress.

In the hexagonal GaN, the experimentally reported DPCs, especially for D3 and D4, are largely scattered [3 – 5]. This large discrepancy among various reports mostly comes from the difference of the definition of DPC used in the analysis of the experimental results. The prototype of DPCs is one defined in the invariant category [1]. In invariant method by Bir and Pikus, the total Hamiltonian (electronic part + lattice part and the interaction part between the both) is invariant under the external or internal stress (strain) application, even if the crystal symmetry is lowered by the applied stress \( f_{\gamma} \) belonging to the irreducible representation \( \Gamma \) and the component \( \gamma \). Therefore, the stress Hamiltonian term \( f_{\gamma} Q_{\gamma} \), where \( Q \) is a normal coordinate, must be transformed into total symmetry in the crystal symmetry. This condition is satisfied only in the case that the both \( f_{\gamma} \) and \( Q_{\gamma} \) transform under the
same irreducible representation. Stress (Strain) is the second rank symmetry tensor, and the six different symmetry tensors, \( xx, yy, zz, xy, yz, \) and \( zx \), should be reduced into adequate irreducible tensors in the invariant method, as well known. The irreducible second-rank symmetry tensors in \( C_{6v} \) group are \( xx + yy, zz, xy, xx – yy, yz, \) and \( zx \) (see the second rank basis of \( C_{6v} \) group in the table of irreducible representation [6]). On analyzing the experimental data in the invariant category, the applied stresses (strains) such as \( xx, yy, \) and \( zz \) must be developed into the irreducible second-rank symmetry tensors. Recent papers sometimes employ the unreduced stress (strain) tensors, which span Cartesian coordinate, to obtain the values of the DPCs from the observed data. These DPCs are the different definition from the DPCs used in the invariant method. Thus, the reported values of the DPCs are scattered. In the framework that the conduction band is formed in an \( s \) orbital of III group and the valence band is composed in \( 2p \) orbital of nitrogen ion, the relationship of the cubic approximation, \( D_3 = -2D_4 [1] \), is absolutely right. The slight gap from \( D_3 = -2D_4 \) may be caused in mixing of other orbital into the relevant valence band state.

In this contribution, we present the correction of the Bir and Pikus matrix in the next section, and furthermore, try to show a revised expression for the DPCs of wurtzite symmetry, following Henry, Schnatterly, and Slichter treatment [7 – 9]. The basic expression will be given.

2. Correction of Bir and Pikus expression

We definitely deal with the ligand field splitting term [6, 10], which arises by mean of the lowered (wurtzite) symmetry from cubic (zinc blende) structure. It is worth paying attention that the trace of the energy matrix for the energy splitting term must be zero, namely a center of gravity of the energy is not shifted on the energy splitting brought about lower symmetry. The equivalent operator \( (J_z^2 - \frac{1}{3}) \) [3, 10] for the \( p \)-like basis should be used to calculate the matrix elements instead of \( J_z^2 \), which is employed by Bir and Pikus, leading to the different band alignment as shown in Fig.1. It should be noticed that the conduction band is also shifted, because \( J_z^2 \psi_c(r) = 0 \) but \( (J_z^2 - \frac{1}{3}) \psi_c(r) \neq 0 \), where \( \psi_c(r) \) is an electron wavefunction in the conduction band.

![Figure 1 Band regime. (a) is predicted by Bir and Pikus scheme, and (b) the present scheme. The suffix 2 indicates that the ligand field splitting term is included. \( \Gamma_1 \) in the upper part indicates the conduction band symmetry, and that in the lower part the valence band symmetry, which is split off by the trigonal ligand field. \( \Delta_1 \) is the ligand field splitting energy.](image)

This correction significantly influences the manner of the determination of the DPCs. Considering the method of determining the DPCs from the viewpoint of experimentalists, the Bir and Pikus scheme (see Fig. 1(a)) can independently provide the DPCs \( D_1 + D_{c1} \) (= \( C_1 \)) and \( D_2 + D_{c2} \) (= \( C_2 \)), where \( D_{c1} \) and \( D_{c2} \) are the DPCs in the conduction band, and which correspond to the totally symmetric deformation, from the hydrostatic pressure and stress dependence of the transition energy from the lowest valence band \( \Gamma_1 \) to the conduction band, because they take no trigonal ligand field part in the \( \Gamma_1 \) (\( p \)) valence band into account. In our corrected scheme (see Fig. 1(b)), the transition energy involves the energy lowered by the trigonal component of the ligand field potential in the band \( \Gamma_1(p) \). Therefore, \( C_1 \) and \( C_2 \) cannot be uniquely determined by the hydrostatic and the stress experiments. Here, the notations of the DPCs are similar to those of Chuang and Chang [11].
In accordance with the above description, we develop a strain matrix that is corrected by definitely including the ligand field splitting parameter $\Delta_1$ into the strain Hamiltonian. We extract only the terms relevant to the strain effects for the valence band to avoid complexity. The total ligand field splitting energy is regarded as $\Delta_1 (= \langle \phi_v(r) | V | \phi_v(r) \rangle$, where $V$ is the potential in a trigonal portion, and $\phi_v(r)$ is the wavefunction of the valence band. The partial ligand field splitting energy of $\frac{1}{3} \Delta_1$ is allotted to the two-fold degenerated band $\Gamma_5(\pi_x, \pi_y)$ and the $-\frac{2}{3} \Delta_1$ to the band $\Gamma_1(\pi_z)$. Hence, the energy gravity is held. Spin-orbit interaction is ignored, because the stress energy is much higher than that of the spin-orbit interaction at an interface of a hetero-structure or a multi-layer composed of materials with different lattice constants.

$$\begin{bmatrix}
A & V & W \\
V & B & W \\
W & W & C
\end{bmatrix}$$  

(1)

$$A = \Delta_0 + (1/3) \Delta_1 + D_1'(zz) \varepsilon_{zz} + D_2'(xx+yy) \varepsilon_{xx+yy} + D_3(xx - yy) \varepsilon_{x-x+y-y},$$

$$B = \Delta_0 + (1/3) \Delta_1 + D_1'(zz) \varepsilon_{zz} + D_2'(xx + yy) \varepsilon_{xx+yy} - D_5(xx - yy) \varepsilon_{x-x+y-y},$$

$$C = \Delta_0 - (2/3) \Delta_1 + D_1''(zz) \varepsilon_{zz} + D_2''(xx + yy) \varepsilon_{xx+yy},$$

$$V = D_3 \varepsilon_{yy},$$

$$W = D_6 \varepsilon_{xz} \text{ or } D_6 \varepsilon_{zx},$$  

(2)

where $D_1'(zz) = D_1 + (1/3)D_3$, $D_2'(xx+yy) = D_2 + (1/3)D_4$, $D_1''(zz) = D_1 - (2/3)D_3$, and $D_2''(xx+yy) = D_2 - (2/3)D_4$. $\Delta_0 = \langle \phi_v(r) | V | \phi_v(r) \rangle$. $V$ is the potential energy of the cubic portion of the potential. Furthermore, the following relations stand,

$$D_1'(zz) - D_1''(zz) = D_3,$$  

(3)

$$D_2'(xx+yy) - D_2''(xx+yy) = D_4.$$  

(4)

The notation of $\varepsilon_{ij}$ implies an irreducible strain. The suffixes of the strains and the functions in the parentheses of $D$’s such as $(xx+yy)$ indicate the $\gamma$th basis functions belonging to irreducible representation $\Gamma$ to clarify the physical meaning of strain much more. For the conduction band, four different DPCs ($D_{c1}(zz)$ and $D_{c2}(xx+yy)$) for $\Delta_0$, and $D_{c3}(zz)$ and $D_{c4}(xx+yy)$ for $\Delta_1$) should be assigned because $\Delta_{c_0} = \langle \phi_c(r) | V | \phi_c(r) \rangle \neq 0$. However, as these four DPCs cannot be determined from the stress experimental results, we can settle four DPCs into two as $D_{c1}(zz)$ and $D_{c1}(xx+yy)$ without any practical problems.

3. Alternative approach to deformation potential of wurtzite symmetry

In the same era, the alternative approach in the invariant category is developed by Henry, Schnatterly, and Slichter (HSS) [7 - 9], who treated cubic symmetry case and showed more understandable physical comprise. We apply HSS treatment to obtain the expression of the DPCs for wurtzite
symmetry. Here, we will discuss an alternative approach to the deformation potentials, based on the treatment by HSS moment method [7 - 9]. We introduce into the one-electron Hamiltonian a system of normal coordinates \( \mathbf{Q}_{\gamma} \), which relate to the lattice normal modes belonging to irreducible representations \( \Gamma \gamma \) and span the eigen-spaces of the phonon modes. It should pay attention to the fact that Hooke’s law, \( f_{\gamma} \propto \Delta \mathbf{Q}_{\gamma} \), makes ends meet directly in this coordination system. This External stresses do not directly affect the electronic state because a stress Hamiltonian contains no electron coordinate \( \mathbf{r} \). On the other, they deform the crystal lattice, and this transformation affects specific lattice normal modes depending on the stress symmetry and deviates the potential \( V(\mathbf{r}, \mathbf{Q}_{\gamma}) \). The deformation of the potential causes alteration of the electronic states through an electron – phonon interaction. We take the extreme condition under which the alteration of the band energy by an applied or internal stress is much stronger than the splitting energy of the spin–orbital interaction, and deal only with the \( \Gamma \) point of the Brillouin zone. To make the role of the phonon clearer, we develop the potential using the normal coordinates \( \mathbf{Q}_{\gamma} \) to the first order.

\[
V(\mathbf{r}, \mathbf{Q}_{\gamma}) = V(\mathbf{r}, \mathbf{Q}_{\gamma} = \mathbf{0}) + \sum \frac{\partial V(r, \mathbf{Q}_{\gamma})}{\partial \mathbf{Q}_{\gamma}} \mathbf{Q}_{\gamma} + \mathbf{Q}_{\gamma} \]

\( \mathbf{Q}_{\gamma} = \mathbf{0} \) implies the equilibrium positions of the crystal lattice. It is full worth noting that \( \frac{\partial V(r, \mathbf{Q}_{\gamma})}{\partial \mathbf{Q}_{\gamma}} \) must be a Hamiltonian operator in real space, and is of the same symmetry as the \( \gamma \)th basis function of \( \Gamma \) (invariant requisition). The second term of Eq. (5) represents the change of the potential energy of electron as a result of the lattice deformation. Now, we add an external stress Hamiltonian \( \mathcal{A}_{\text{stres}}(\mathbf{Q}_{\gamma}) = -\Sigma f_{\gamma}^{} \mathbf{Q}_{\gamma} \) to Eq. (5), where \( f_{\gamma} \) must be a force of with the same symmetry as the lattice normal mode. This compulsion is also an invariant requisition. The lattice normal mode Hamiltonian \( \mathcal{A}_{\gamma}'(\mathbf{Q}) = \Sigma \{P^2/(2M) + \frac{1}{2}M\omega^2\mathbf{Q}_{\gamma}^2\} \) will be modified by the external stresses, where \( P \) is momentum, \( M \) mass, and \( \omega \) frequency of the lattice normal mode. The external stresses cause rearrangement of the equilibrium position of the lattice normal mode as follows,

\[
\frac{1}{2}M\omega^2\mathbf{Q}_{\gamma}^2 - f_{\gamma}^{} \mathbf{Q}_{\gamma} = \frac{1}{2}M\omega^2(\mathbf{Q}_{\gamma}'^{} - f_{\gamma}^{}M\omega^2)^2 - \frac{1}{2}f_{\gamma}^2/(M\omega^2).
\]

The new equilibrium position of the lattice mode under stress is given as

\[
\mathbf{Q}_{\gamma}'^{} = \mathbf{Q}_{\gamma}^{} - \mathbf{f}_{\gamma}^{}M\omega^2 = \mathbf{Q}_{\gamma}^{} - \Delta \mathbf{Q}_{\gamma}^{} \quad (\Delta \mathbf{Q}_{\gamma}^{} = f_{\gamma}^{}M\omega^2),
\]

\( \Delta \mathbf{Q}_{\gamma} \) means a strain transformed under an irreducible representation \( \Gamma \gamma \). Substituting Eq. (7) into Eq. (5),

\[
V(\mathbf{r}, \mathbf{Q}_{\gamma}') = V(\mathbf{r}, \mathbf{Q}_{\gamma}') + \sum \frac{\partial V(r, \mathbf{Q}_{\gamma}')}{\partial \mathbf{Q}_{\gamma}'} \mathbf{Q}_{\gamma}' \bigg|_{\mathbf{Q}_{\gamma}' = \Delta \mathbf{Q}_{\gamma}}
\]

Here, we take the coordinate origin at the new equilibrium position. The stress Hamiltonian perturbing the electronic state can be rewritten using the new coordinate \( \mathbf{Q}_{\gamma}' \) and the irreducible strain amplitude \( \Delta \mathbf{Q}_{\gamma} \).

\[
\mathcal{A}_{\text{stres}}(\mathbf{Q}_{\gamma}') = \Sigma \delta V'(r, \mathbf{Q}_{\gamma}')?>\Delta \mathbf{Q}_{\gamma}'
\]

where \( \delta V'(r, \mathbf{Q}_{\gamma}') = \frac{\partial V(r, \mathbf{Q}_{\gamma}')}{{\partial \mathbf{Q}_{\gamma}'}} \bigg|_{\mathbf{Q}_{\gamma}' = \Delta \mathbf{Q}_{\gamma}}. \]

Hence, these descriptions clarify that the external stresses modify the lattice equilibrium positions, resulting in the change of electronic states through the linear term Eq. (5) of the electron-phonon interaction (see Refs. [7 – 9] for details).

Particular attention that \( \Delta \mathbf{Q}_{\gamma} \) is the irreducible strain labeled “\( \gamma \)”, which transforms in the same form as the stress \( f_{\gamma} \) under \( C_6v \) symmetry operations should be paid. Thus, the stress matrix
element can be represented as $\langle \chi_v(r) \ | \ \mathcal{H}_{\text{stress}}(Q_{\Gamma\gamma}) \ | \ \chi_v(r) \rangle$. Assuming a linear relation between stress and strain, $f_{\Gamma\gamma} \propto \Delta Q_{\Gamma\gamma}$ (Hooke’s law),

$$<\chi_v(r) \ | \ \Sigma \delta V'(r, Q_{\Gamma\gamma}') \ | \ \chi_v(r)> \Delta Q_{\Gamma\gamma} = \Sigma K_{\Gamma\gamma} <\chi_v(r) \ | \ \delta V'(r, Q_{\Gamma\gamma}') \ | \ \chi_v(r)> f_{\Gamma\gamma}, \quad (11)$$

where $\chi_v(r)$ represents a $p$-like wave function of the valence band, and transforms according to the irreducible representation $A_1$ or $E_1$ under $C_{6v}$ symmetry operations. $K_{\Gamma\gamma}$ is a proportional constant between an external stress ($f_{\Gamma\gamma}$) and the resulting strain ($\Delta Q_{\Gamma\gamma}$). It should again be emphasized that in normal coordinate space, strains are linearly connected to stresses by Hooke’s law.

There are six ways to externally squeeze a crystal. For hexagonal symmetry $P\overline{6}3mc$, these are classified into four types in accordance with reducing the second rank tensors under $P\overline{6}3mc$ symmetry as follows:

$$\{A_1 + E_1\} \otimes \{A_1 + E_1\}_{\text{symmetry}} = \{A_1\}^a_{zz} + \{E_1\}^a_{xx+yy} + E_1(xz, yz) + E_2(xx-yy, xy). \quad (12)$$

Three anti-symmetric second-rank tensors are removed, because the stresses (strains) are symmetric. The functions in the parentheses indicate the basis functions transforming under each irreducible representation. Each stress type must be assigned to one deformation potential constant. Hence, there should be four different deformation potential constants in each band for hexagonal symmetry $P\overline{6}3mc$ at the maximum. By substituting Eq. (12) into Eq. (11), we can define the new DPCs in a form directly responsible to stresses. For $\Gamma_5(E_1)$ band,

$$<\chi_v(r) \ | \ \Sigma \delta V'(r, Q_{\Gamma\gamma}') \ | \ \chi_v(r)> f_{\Gamma\gamma} = \Sigma D_{\Gamma\gamma}(\Theta_{\Gamma\gamma})_{vu} f_{\Gamma\gamma}, \quad (13)$$

where $\chi_v(r)$ is an electron wavefunction, and for the valence band of nitride semiconductors, $v$ ($u$) is a $p_z$ or $p_x$ orbital (vice versa), and $(\Theta_{\Gamma\gamma})_{vu}$ is a tensor matrix element [7] obeying the following relations.

$$\Sigma (\Theta_{\Gamma\gamma})_{vu} \cdot (\Theta_{\Gamma'\gamma'})_{uv} = A_\Gamma \delta_{\Gamma\Gamma'} \delta_{\gamma\gamma'}. \quad (14)$$

$A_\Gamma$ is a constant depending on $\Gamma$ only. The sum runs over $v$ and $u$, and

$$\Sigma (\Theta_{\Gamma\gamma})_{vv'} (\Theta_{\Gamma'\gamma'})_{uu'} = \delta_{vw'}, \quad (15)$$

where the sum also runs over $v$ and $\Gamma$.

For $\Gamma_1(z)$ ($A_1(z)$) band, the same expression as Eq. (13) stands, but independently. As a cross-strain (shear strain) term,

$$D_{\text{cross}}(zx) = D_{\text{cross}}(yz) = <\chi_v(p_z) \ | \ \delta V'(zx) \ | \ \chi_v(p_z) >. \quad (16)$$

Any external stresses must be decomposed into the above irreducible stress components to analyze observed data. For analysis of the experimental observations, the concrete representation will be exhibited elsewhere.

For the case of lattice mismatch in hetero-structure, the band alignment is significantly influenced by the internal stresses caused by the lattice mismatch.

4. Summary

Bir and Pikus’s strain matrix for semiconductors with wurtzite structure (hexagonal symmetry) was re-examined, and corrected by properly adopting the trigonal part of the ligand field term. Introducing a
normal coordinate system, an alternative approach to the deformation potential is tried in the 
framework of invariant regime. The basic expressions of the DPCs for the valence band of nitride 
semiconductors are given. This definition connecting to not strain but stress is formalised, makes its 
physical situation more evident, and is much more straightforward for experimentalist.

References
[1] Bir G L, and Pikus G E 1974 Symmetry and Strained-Induced Effects in Semiconductors 
translated from Russian by P. Shelnitz (New York and Toronto, John Wiley & Sons, Inc.), 
and references therein
[2] Banal R, Funato M and Kawakami Y 2009, Phys. Rev. B79 121308(R)
[3] Peng H Y, McCluskey M D, Gupta Y M, Kneissl M and Johnson N M 2005 Phys. Rev. B71 
115207
[4] Ishii R, Kaneta A, Funato M and Kawakami Y 2010, Phys. Rev. B81 155202
[5] Wagner J M and Bechstedt F 2002 Phys. Rev. B66 115202
[6] Griffith J S 1962 The Irreducible Tensor Method for Molecular Symmetry Group (New York, 
Prentice-Hall)
[7] Henry R C H, Schnatterly S E and Slichter C P, 1965 Phys. Rev. 137 130
[8] Schnatterly S E, 1965 Phys. Rev. 140 A1364
[9] Henry R C H and Schnatterly S E 1968 Physics of Color Center edited by Fowler W B (New 
York and London, Academic Press) chap. 6.
[10] Kamimura H, Sugano S and Tanabe Y 1988 Ligand Field Theory and Its Application (Tokyo, 
Syokabo) (in Japanese).
[11] Chuang S L and Chang C S 1996 Phys. Rev. B54 2491