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First-principles study of 6H-AlN under various pressure conditions

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Abstract. We calculated the electronic and lattice properties of 6H-AlN under various pressure conditions. The pressure conditions are hydrostatic, biaxial, and uniaxial compression and expansion. The 6H polytype has two structures. One is ABCBCB (ABC notation) and the other is ABCACB. 6H-AlN(ABCBCB) is energetically more favorable than 6H-AlN(ABCACB). Symmetry and hexagonality ($H\%$) of 6H-AlN(ABCBCB) are $P\overline{3}m1$ and $67\%$, respectively. The electronic band structures of 6H-AlN polytypes under the ambient pressure show indirect band gaps. The band gap of 6H-AlN(ABCBCB) is closer to direct than that of 6H-AlN(ABCACB). The lattice properties of 6H-AlN(ABCBCB) under the various pressure conditions were optimized automatically by the first-principles molecular dynamics (FPMD) method. We also calculated the electronic band structures, the band gap values, the valence band maximum (VBM), and conduction band minimum (CBM) of 6H-AlN(ABCBCB) under the various pressure conditions. Their electronic band structures are non-metallic and band gaps are indirect with the exception of a few cases. The indirect band gap transforms to direct under expansion conditions.

1. Introduction
6H-AlN has been synthesized by D. M. Schaadt, et al. [1] and the stacking sequence of CBCACB has been observed by L. Zhou, et al. [2]. “CBCACB” is the ABC notation [3, 4]. The CBCACB structure is equal to ABCBCB which was calculated in our previous study [5]. The electronic properties of 6H-AlN are not clear experimentally in detail [1, 2]. We have investigated the electronic and lattice properties of BN, SiC, and AlN polytypes [5, 6, 7]. In the previous study [5, 7], we have calculated the band gaps of BN and AlN polytypes (2H $\sim$ 6H, and 10H). These polytypes are $sp^3$-bonded compounds which consist of hexagonal cation and anion layers in a unit cell and their possible symmetries are $P6_3mc$ and $P3m1$ [3, 4]. Their lattice properties were optimized automatically by the first-principles molecular dynamics (FPMD) method. Most band gaps of them under the ambient pressure are indirect although BN and AlN compounds are wide band gap materials. The purpose of our previous studies [7] is to search the polytype with a direct band gap. We have discussed how to realize the direct band gap in polytypes [7] under the ambient pressure. It was expected that band gaps of $p$H-AlN ($p > 6$) may be direct because that of 2H-AlN is direct [8, 9, 10, 11, 12, 13, 14] and that of 6H-AlN(ABCBCB) is closest to the direct band gap in the calculated polytypes (3H $\sim$ 6H) [5]. As for 10H-AlN [7], calculated band gaps are still indirect. The 6H polytype has two structures as ABCBCB and ABCACB [15] and ABCBCB is energetically more favorable than ABCACB in AlN [5] under the ambient pressure. Very recently, 6H-AlN(ABCBCB) has been calculated by Y. C. Cheng, et al. [16] and its band...
gap is direct. This is inconsistent with our results. The optimized lattice constants [16] are slightly smaller than our results and the electronic band structure of 6H-AlN(ABCBCB) may be sensitive to lattice properties. Therefore, it is expected that the direct band gap will be realized under compression. We investigated 6H-AlN(ABCBCB) under the various compression and expansion conditions, and their electronic properties have been definitively established in this study.

It is important to search wide band gap materials with the ultraviolet region ($\sim 6$ eV). The minimum band gap values of AlN [17, 18] are approximately 6 eV in experiment. The direct band gap is required because it is expected a higher efficiency of luminescence than the indirect band gap. In our previous calculations, the band gaps of 6H-AlN(ABCBCB) [5], 10H-AlN(ABCBCACBCB) [7], and 10H-AlN(ABABABABAC) [7] are close to direct although they are still indirect. Their energy differences of $\Delta_1$ and $\Delta_2$ are 0.23 eV, 0.15 eV, and 0.19 eV, respectively. These values are smaller than that of 3C-AlN with 1.05 eV [5, 7]. $\Delta_1$ and $\Delta_2$ are the minimum band gap and minimum direct band gap, respectively. In particular, the energy difference of $\Delta_1$ and $\Delta_2$ could be sensitive to the lattice properties when it is quite small. It may be possible to realize the direct band gap for 6H- and 10H-AlN polytypes using an external perturbation as a pressure. As for 3C-AlN, we have investigated the change in the band gap properties under hydrostatic expansion [5]. The band gap of 3C-AlN is direct under $P = -31.3$ GPa [5] which corresponds to the lattice expansion with 8.7 % on the comparison with the equilibrium lattice constant. It is still indirect under $P = -14.1$ GPa (lattice expansion with 2.7 %). The lattice expansion with 8.7 % is quite difficult actually.

One of the authors (K. Kobayashi) has been investigated the electronic properties of 2H-BN under anisotropic compression [14]. The indirect band gap in 2H-BN is invariant under uniaxial compression along $c$-axis ($P_z = 300$ GPa) because the energy difference of $\Delta_1$ and $\Delta_2$ under $P = 0$ GPa is quite large with 3.36 eV [5]. A definition of $P$ and $P_z$ will be described in the next section. In contrast, the energy differences of $\Delta_1$ and $\Delta_2$ for 6H-AlN(ABCBCB) are 0.23 eV. We focus on 6H-AlN(ABCBCB) due to smaller lattice constants although the energy difference of $\Delta_1$ and $\Delta_2$ for 10H-AlN are smaller. This is more suitable to compare with the results of 6H-AlN by Y. C. Cheng, et al. [16]. Smaller lattice properties lead to lower consuming the computer resources. In this sense, it is suitable to treat 6H-AlN(ABCBCB) and it is expected that the direct band gap will be realized more easily in 6H-AlN(ABCBCB) applying under the various pressure conditions because of the small energy difference of $\Delta_1$ and $\Delta_2$. We have also evaluated the electronic properties (valence band maximum [VBM], conduction band minimum [CBM], band gap values, direct or indirect) of 6H-AlN(ABCBCB) under the various pressure conditions in this study.

2. Method of Calculation

The present calculation is based on the local density approximation (LDA) in density functional theory [19, 20] (DFT) with the von-Barth and Hedin (BH) interpolation formula [21] for the exchange-correlation. The Wigner (W) [22], and Perdew and Zunger (PZ) [23] interpolation formulae for the exchange-correlation are also used in order to compare with the results using BH. The symmetry, hexagonality, Zhidanov [3, 4], and h-c [3, 4] notations of 6H-AlN(ABCBCB) which treats in this study are $P3m1$, 67 %, 2112, and $hhhc$, respectively. Hexagonality is the ratio of the number of $h$ character and the total number of $c$ and $h$ characters in the unit cell [5] as shown in Fig. 1. The number of atoms in the unit cell is 12 (six Al atoms and six N atoms). The details of the 6H-AlN polytype were reported in our previous study [5]. The optimized pseudopotentials by Troullier and Martins (TM) [24, 25] are used for Al and N. Nonlocal parts of the pseudopotentials are transformed to the Kleinman-Bylander separable forms [26] without ghost bands. A partial core correction (PCC) [27] is considered for the Al pseudopotential. Mesh sizes of sampling k-points in an irreducible Brillouin zone (BZ) are $12 \times 12 \times 2 \sim 12$.
The total energy difference between $12 \times 12 \times 2$ and $12 \times 12 \times 8$ is less than approximately 0.1 meV/Al$_2$N$_2$. A convergence of lattice parameters is sufficient at the $12 \times 12 \times 2$ mesh because 6H-AlN(ABCBCB) is non-metallic under all pressure conditions in this study and lattice constant $c$ is large in the 6H polytype. The structural optimization using FPMD is performed at the $12 \times 12 \times 2$ mesh. $12 \times 12 \times 8$ is used in order to obtain more detailed electronic properties (VBM, CBM, and electronic band structures). The wave function is expanded in plane waves and the cutoff energy is 144 Ry in all calculated structures. As for the cutoff energy, a sufficient convergence in hexagonal-BN (h-BN) was obtained at 144 Ry in the previous study [28]. The structural optimization of internal atoms in the unit cell was performed using Hellmann-Feynman forces. Our criterion for optimizing the internal coordinates is that the maximum force acting on each atom should be less than $2.0 \times 10^{-4}$ Ry/Bohr.

$$\sigma_{\alpha\beta} = \frac{1}{\Omega} \frac{\partial E_{\text{tot}}}{\partial \epsilon_{\alpha\beta}},$$

where $\sigma_{\alpha\beta}$ is a stress tensor, $\alpha, \beta$ denote Cartesian coordinates (x, y, z), $\Omega$ is the volume of the unit cell, $E_{\text{tot}}$ is the total energy and $\epsilon$ is the strain. The cell parameters are tuned by coincidence of internal and external pressures ($P_{\text{int}}, P_{\text{ext}}$) in the process of FPMD as follows,

$$P_{\text{int}} = -P_{\text{ext}}.$$  

In this study, we define a positive (negative) value of $P_{\text{ext}}$ indicates compression (expansion) and “ext” is omitted hereafter. We examined the hydrostatic, biaxial ($a, b$-axis), and uniaxial ($c$-axis) compression and expansion conditions.

Hydrostatic compression ($\sigma_{xx} = \sigma_{yy} = \sigma_{zz} < 0$) and expansion ($\sigma_{xx} = \sigma_{yy} = \sigma_{zz} > 0$) are defined as

![Figure 1. Crystal structure (unit cell) of 6H-AlN(ABCBCB).](image)

The cubic and hexagonal characters of the cation-anion bilayers are indicated by “c” and “h”. The third-neighbor cation-anion atoms are indicated by arrows. The arrows of $P_{\text{xy}}$ and $P_{\text{z}}$ indicate the direction of each pressure (compression and expansion). The hydrostatic pressure condition is $P_{\text{xy}} = P_{\text{z}} = 0$, the biaxial pressure condition is $P_{\text{xy}} \neq 0$ and $P_{\text{z}} = 0$, and the uniaxial pressure condition is $P_{\text{xy}} = 0$ and $P_{\text{z}} \neq 0$. Internal stresses [29] were obtained by the following formula,
\[ P = -\sigma_{xx} = -\sigma_{yy} = -\sigma_{zz}. \]  
\[ \text{(3)} \]

Biaxial compression (\( \sigma_{xx} = \sigma_{yy} < 0 \)) and expansion (\( \sigma_{xx} = \sigma_{yy} > 0 \)) in the \( a, \ b \)-plane (\( a, \ b \)-axis) are defined as

\[ P_{xy} = -\sigma_{xx} = -\sigma_{yy}, \]  
\[ \text{(4)} \]

when the pressure of \( P_z = 0 \) GPa.

Uniaxial compression (\( \sigma_{zz} < 0 \)) and expansion (\( \sigma_{zz} > 0 \)) along \( c \)-axis are defined as

\[ P_z = -\sigma_{zz}, \]  
\[ \text{(5)} \]

when the pressures of \( P_{xy} = 0 \) GPa. \( P_{xy} \) and \( P_z \) are indicated by arrows in Fig. 1. Our criterion for optimizing the unit cell surfaces is that the maximum pressure acting on each unit cell surface should be less than 0.03 GPa, which corresponds to an alteration of less than 0.001 \( \text{\textg{\textm{\text{\texta{A}}}}} \) in the optimization of the lattice constant. Off-diagonal terms of the stress tensor were not considered in this study.

Rhombohedral lattice structures, impurities, defects, stacking faults and intercalation were not calculated in this study. Structural phase transition, crystallinity break, interlayer gliding, etc. were not considered in the process of the FPMD. The crystal symmetry and the number of k-points in each phase was kept during the cell optimization in this study. Although the pseudopotentials used in the FPMD calculation do not take into account the effect of core electrons with the exception of PCC for Al, the influence of core states is small in this study.

3. Results and Discussion

3.1. Lattice properties

The optimized lattice properties of 6H-AlN(ABCBCB) under the various compression and expansion conditions are tabulated in Table 1. The directions of applied pressures as hydrostatic (\( P \)), biaxial (\( P_{xy} \)), and uniaxial (\( P_z \)) are indicated by arrows in Fig. 1. We have investigated 6H-AlN(ABCBCB) under \( P = -7 \) GPa \( \sim 5 \) GPa, \( P_{xy} = -10 \) GPa \( \sim 10 \) GPa, and \( P_z = -20 \) GPa \( \sim 10 \) GPa. Theoretical equilibrium lattice constants \[16\] of 6H-AlN are also tabulated and they agree well with our results. They are smaller by approximately 1.0 % than our results. Atomic displacements of internal parameters from the ideal positions in the 6H-AlN(ABCBCB) under the various pressure conditions are quite small, within approximately 0.1% of lattice constant \( c \).

In experiment, the detailed structures have not been determined definitely although the stacking sequence of CBCACB and the \( P_3m1 \) symmetry in 6H-AlN has been observed by L. Zhou, et al. \[2\]. This stacking sequence (CBCACB) is equal to the ABCBCB structure treated in this study.

We calculated the electronic and structural properties of 6H-AlN(ABCBCB) using other LDA formulae with W \[22\] and PZ \[23\] in order to compare with those using the BH \[21\] formula. The equilibrium lattice constants in PZ are slightly larger by approximately 0.1 % than those in BH. In contrast, the lattice constants in W are larger by 1 % than those in BH. We also calculated the electronic and structural properties of 6H-AlN(ABCBCB) using the Al pseudopotential without PCC \[27\] in order to compare with the results considered with PCC. The equilibrium lattice constants without PCC are slightly shorter than those with PCC. Furthermore, we calculated the electronic properties of 6H-AlN(ABCBCB) using the lattice constants obtained by Y. C. Cheng, et al \[16\]. Two cases are treated in this calculation. One uses internal coordinates without a structural optimization, the other uses those with the structural optimization of internal ionic coordinates in the unit cell. In both cases, the unit cell is fixed. These results are also tabulated in Table 1.
Table 1. Optimized lattice constants $a$ and $c/\text{Å}$, and the $c/a$ ratios of 6H-AlN(ABCBCB) under the various compression and expansion conditions. $p$ is the number of Al-N bilayers in the unit cell. $p$ is 6 in the 6H polytype. “[PZ]” and “[W]” indicate Wigner [22], and Perdew and Zunger [23] interpolation formulae, respectively. “[No PCC]” indicates using the pseudopotential without PCC [27]. “[th]” indicates the results by Y. C. Cheng, et al [16]. $\Omega$ (Å$^3$) is the unit cell volume.

| 6H-AlN(ABCBCB)          | $c$   | $c/p$ | $a$    | $c/a$ | $\Omega$ |
|-------------------------|-------|-------|--------|-------|----------|
| 6H-AlN($P = 0$ GPa)     | 15.059| 2.510 | 3.108  | 4.846 | 125.96   |
| 6H-AlN($P = 0$ GPa)[PZ] | 15.086| 2.514 | 3.113  | 4.846 | -        |
| 6H-AlN($P = 0$ GPa)[W]  | 15.224| 2.537 | 3.139  | 4.850 | -        |
| 6H-AlN($P = 0$ GPa)[No PCC] | 15.019| 2.503 | 3.100  | 4.845 | -        |
| 6H-AlN($P = 5$ GPa)     | 14.893| 2.489 | 3.085  | 4.842 | 123.07   |
| 6H-AlN($P = -5$ GPa)    | 15.194| 2.532 | 3.134  | 4.849 | 129.22   |
| 6H-AlN($P = -7$ GPa)    | 15.253| 2.542 | 3.145  | 4.850 | 130.65   |
| 6H-AlN($P = 0$ GPa)[th [16]] | 14.89 | 2.48 | 3.07 | 4.85 | -        |
| 6H-AlN($P = 5$ GPa)     | 14.936| 2.489 | 3.085  | 4.842 | 123.07   |
| 6H-AlN($P = -5$ GPa)    | 15.194| 2.532 | 3.134  | 4.849 | 129.22   |
| 6H-AlN($P = -7$ GPa)    | 15.253| 2.542 | 3.145  | 4.850 | 130.65   |
| 6H-AlN($P = 0$ GPa)[Pxy = 10 GPa] | 15.202| 2.534| 3.047| 4.989| 122.25 |
| 6H-AlN($Pxy = -5$ GPa)  | 14.976| 2.496 | 3.142  | 4.767 | 128.02   |
| 6H-AlN($Pxy = -7$ GPa)  | 14.940| 2.490 | 3.156  | 4.734 | 128.89   |
| 6H-AlN($Pxy = -10$ GPa)| 14.883| 2.480 | 3.179  | 4.682 | 130.25   |
| 6H-AlN($Pz = 10$ GPa)   | 14.626| 2.438 | 3.127  | 4.678 | 123.83   |
| 6H-AlN($Pz = 5$ GPa)    | 14.848| 2.475 | 3.116  | 4.764 | 124.89   |
| 6H-AlN($Pz = -10$ GPa)  | 15.469| 2.578 | 3.093  | 5.001 | 128.19   |
| 6H-AlN($Pz = -15$ GPa)  | 15.674| 2.612 | 3.087  | 5.077 | 129.39   |
| 6H-AlN($Pz = -17$ GPa)  | 15.757| 2.626 | 3.085  | 5.107 | 129.89   |
| 6H-AlN($Pz = -20$ GPa)  | 15.884| 2.647 | 3.082  | 5.154 | 130.66   |

3.2. Electronic band structures

All calculated electronic band structures in this study are non-metallic. The minimum band gap ($\Delta_1$) and minimum direct band gap ($\Delta_2$) of 6H-AlN(ABCBCB) under the various pressure conditions are tabulated in Table 2. It should be noted that these values ($\Delta_1$) are underestimated in the DFT-LDA calculations. In contrast, a band gap feature as indirect or direct is well reproduced in the DFT calculations with the exception of a few cases [28, 30]. VBM is at the $\Gamma$ point with the exception of $Pxy = 10$ GPa and $Pz = -10$ GPa. This is a typical feature of $p$-states in $sp^3$-bonded III-V and VI-VI compounds. VBM of 6H-AlN(ABCBCB) under $Pxy = 10$ GPa and $Pz = -10$ GPa are the $\Gamma$ point on the $\Gamma$ - $A$ line. CBM of all calculated cases in 6H-AlN(ABCBCB) are the $L$ point, when their band gaps are indirect. The hexagonal Brillouin zone is shown in Fig. 2(a). The electronic band structures of 6H-BN(ABCBCB) under $P = 5$, 0, -7 GPa, $Pxy = -10$ GPa, and $Pz = -20$ GPa are shown in Figs. 2(b) - (f), respectively. Their valence band maximum (VBM) - conduction band minimum (CBM) are tabulated in Table 2. The electronic band structures of 6H-AlN(ABCBCB) under compression and expansion conditions resemble each other remarkably from Figs. 2(b) - (f), although dispersions of individual bands differ slightly among them. The bottom bands of the conduction states in Figs. 2(b) - (f) are not degenerated at the $\Gamma$ point. The top band of the valence states in Fig. 2(f) is doubly degenerated at the $\Gamma$ point. In Figs. 2(b) - (e), they are not degenerated. The $\Gamma$ point has $C_{3h}$ symmetry in 6H-AlN(ABCBCB, $P3m1$). The doubly degenerated bands belong to the E representation. If initial or final states belong to this representation, a direct transition is allowed [31]. The non-degenerated highest occupied and lowest unoccupied bands at the $\Gamma$ point belong to the $A_1$ representation. If initial and final states belong to this representation, the direct transition is
also allowed [31].

Figure 2. Hexagonal Brillouin zone (a) and electronic band structures (b) - (f) of 6H-AlN(ABCBCB) under $P_e = 5 \text{ GPa}$, $0 \text{ GPa}$, $-7 \text{ GPa}$, $P_{xy} = -10 \text{ GPa}$, and $P_z = -20 \text{ GPa}$. The band gaps under $P = -7 \text{ GPa}$ (d), $P_{xy} = -10 \text{ GPa}$ (e), and $P_z = -20 \text{ GPa}$ (f) are direct.

As for 6H-AlN(ABCBCB) there are no experimental and theoretical reports under the compression or expansion conditions. At the first, we expected that the direct band gap would be realized under compression conditions. In fact, the energy difference of $\Delta_1$ and $\Delta_2$ ($|\Delta_1 - \Delta_2|$) for 6H-AlN(ABCBCB) increases with increasing the pressure ($P$, $P_{xy}$, and $P_z$). This means the indirect band gap is enhanced under compression. It was found that the indirect band gap transforms to direct under expansion from Table 2. $|\Delta_1 - \Delta_2|$ decreases with decreasing the pressure and the direct band gap as $|\Delta_1 - \Delta_2| = 0$ is realized under expansion. This transition occurs under all calculated expansion conditions as $P$, $P_{xy}$, and $P_z$. The transition pressure ranges from indirect to direct under $P$, $P_{xy}$, and $P_z$ are $-5 \sim -7 \text{ GPa}$, $-7 \sim -10 \text{ GPa}$, and $-17 \sim -20 \text{ GPa}$, respectively. The value of $P_z$ (= -20 GPa) is three times larger than that of $P$ (= -7 GPa). The unit cell volumes under $P = -7 \text{ GPa}$, $P_{xy} = -10 \text{ GPa}$, and $P_z = -20 \text{ GPa}$ are almost similar to each other in the range of 130.25 $\sim$ 130.66 Å$^3$ from Table 1. This show the transition from indirect to direct occurs at the nearly equal volume range under each expansion condition.

The band gaps of 6H-AlN(ABCBCB) using other LDA formulae of W and PZ under $P = 0 \text{ GPa}$ are indirect and those without PCC and using the lattice constants by Y. C. Cheng, et al [16] are also indirect as shown in Table 2. The band gap using the W formula in LDA is nearly direct with $|\Delta_1 - \Delta_2| = 0.03 \text{ eV}$ since the equilibrium lattice constants are larger by 1 % than those using the BH formula and it corresponds to lattice expansion. These larger lattice constants are close to those under $P = -7 \text{ GPa}$ within 0.2 %, in which the band gap is direct.

Covalency of the AlN polytype is weaker than that of the BN polytype [5]. We calculated the total charge densities of 6H-AlN(ABCBCB) under the various pressure conditions. An amount of the charge density inside the sphere (radius = 1.0 a.u. = 0.529 Å) around each atom slightly decreases with decreasing the pressure. This radius (= 1.0 a.u.) is adopted because it
Table 2. Electronic properties of calculated 6H-AlN(ABCBCB) under the various compression and expansion conditions. Previous results [5, 7] of 2H, 4H, 10H, and 3C-AlN are also tabulated. Δ₁ and Δ₂ indicate the minimum band gap (eV) and minimum direct band gap (eV), respectively. The values of Δ₁ are underestimated in the DFT-LDA calculation. Parentheses in the Δ₂ column indicate the k-point of the minimum direct band gap. “[PZ]” and “[W]” indicate Wigner [22], and Perdew and Zunger [23] interpolation formulae, respectively. “[No PCC]” indicates using the pseudopotential without PCC [27]. “[ideal]” and “[optimized]” indicate that the lattice constants [16] are used in this study with ideal internal coordinates of ions in the unit cell and structurally optimized ones, respectively. “[th]” indicates the results by Y. C. Cheng, et al [16]. H indicates hexagonality (%).

|          | Δ₁     | Δ₂     | VBM - CBM | H (%) |
|----------|--------|--------|-----------|-------|
| 10H-AlN(ABCBCACBCB) indirect | 4.15   | 4.30 (Γ) | Γ-U   | 60    |
| 6H-AlN(ABCACB) indirect | 3.74   | 4.27 (M) | Γ-M   | 33    |
| 6H-AlN(ABCBCB) indirect | 4.06   | 4.30 (Γ) | Γ-L   | 67    |
| 6H-AlN(ABCBCB)[PZ] indirect | 4.04   | 4.24 (Γ) | Γ-L   | 67    |
| 6H-AlN(ABCBCB)[W] indirect | 3.90   | 3.93 (Γ) | Γ-L   | 67    |
| 6H-AlN(ABCBCB)[No PCC] indirect | 4.11   | 4.43 (Γ) | Γ-L   | 67    |
| 6H-AlN(ABCBCB)[ideal] indirect | 4.15   | 4.69 (Γ) | Γ-L   | 67    |
| 6H-AlN(ABCBCB)[optimized] indirect | 4.12   | 4.63 (Γ) | Γ-L   | 67    |
| 6H-AlN(P = 5 GPa) indirect | 4.09   | 4.50 (Γ) | Γ-L   | 67    |
| 6H-AlN(P = -5 GPa) indirect | 4.03   | 4.07 (Γ) | Γ-L   | 67    |
| 6H-AlN(P = -7 GPa) direct | 3.97   | 3.97 (Γ) | Γ-G   | 67    |
| 6H-AlN(Pxy = 10 GPa) indirect | 4.06   | 4.57 (Γ) | Δ-L   | 67    |
| 6H-AlN(Pxy = -5 GPa) indirect | 3.97   | 4.05 (Γ) | Γ-L   | 67    |
| 6H-AlN(Pxy = -7 GPa) indirect | 3.94   | 3.95 (Γ) | Γ-L   | 67    |
| 6H-AlN(Pxy = -10 GPa) direct | 3.79   | 3.79 (Γ) | Γ-G   | 67    |
| 6H-AlN(Pz = 10 GPa) indirect | 3.92   | 4.21 (Γ) | Γ-L   | 67    |
| 6H-AlN(Pz = 5 GPa) indirect | 4.00   | 4.27 (Γ) | Γ-L   | 67    |
| 6H-AlN(Pz = -10 GPa) indirect | 4.00   | 4.15 (Γ) | Δ-L   | 67    |
| 6H-AlN(Pz = -15 GPa) indirect | 3.89   | 3.96 (Γ) | Γ-L   | 67    |
| 6H-AlN(Pz = -17 GPa) indirect | 3.85   | 3.88 (Γ) | Γ-L   | 67    |
| 6H-AlN(Pz = -20 GPa) direct | 3.78   | 3.78 (Γ) | Γ-G   | 67    |
| 4H-AlN(ABC) indirect | 3.95   | 4.30 (Γ) | Γ-M   | 50    |
| 2H-AlN(AB) direct | 4.31   | 4.31 (Γ) | Γ-G   | 100   |
| 3C-AlN indirect | 3.24   | 4.29 (Γ) | Γ-X   | 0     |
| 6H-AlN(ABCBCB)[th [16]] direct | 4.26   | 4.26 (Γ) | Γ-G   | 67    |
| 4H-AlN(ABC)[th [16]] indirect | 4.15   | -       | Γ-M   | 50    |

corresponds to the atomic radius of N (= 0.53 Å). The amount of the charge density around the Al atom (approximately 0.04 ~ 0.05) is quite smaller than that around B (approximately 0.4) in the BN polytype because ionicity of the AlN polytype is larger than that of BN. It is not clear whether the band gap feature in 6H-AlN(ABCBCB) under the pressure has the relation with the properties of charge densities. The lattice expansion leads to reducing a bond charge around each atom. It is likely that the lowest unoccupied band at the Γ point, which is an anti-bonding state, shifts to lower energies under expansion since the $sp^3$-bonding becomes weaker due to the lattice expansion.
4. Summary
We have calculated the electronic and lattice properties of 6H-AlN(ABCBCB) under the various pressure conditions using FPMD. Hydrostatic ($P$), biaxial ($P_{xy}$), and uniaxial ($P_z$) are treated in this study. We have obtained the electronic band structures, the band gap values ($\Delta_1$, $\Delta_2$), and VBM - CBM of 6H-AlN(ABCBCB) under various pressure conditions. The detailed electronic band structures under the negative - positive pressure range (-20 ~ 10 GPa) have been clarified in this study and they are non-metallic and similar to each other. VBM of all calculated structures are $\Gamma$ with the exception of a few cases. VBM under $P_{xy} = 10$ GPa and $P_z = -10$ GPa are $\Lambda$ on the $\Gamma$-$A$ line. CBM of most calculated structures are the $L$ point with the exception of the direct band gap ($\Gamma$) cases. We have found that the transition of the band gap from indirect to direct occurs under hydrostatic, uniaxial, and biaxial expansion conditions. The indirect band gap is enhanced under compression and $|\Delta_1 - \Delta_2|$ increases with increasing the pressure. A clear guide is given for realizing the direct band gap and it is possible to predict the direct band gap under expansion in the AlN polytypes.

Although the direct band gap in 6H-AlN(ABCBCB) is realized under expansion, it is quite difficult and unrealistic to expand lattice constants in experiment. The inconsistency of the direct [16] and indirect [5] band gaps in 6H-AlN(ABCBCB) is not resolved in this study. It needs further consideration with the electronic properties of 6H-AlN(ABCBCB) using the other functional as GGA (Generalized gradient approximation) in the future task. Another next task is to investigate electronic and lattice properties of larger number of stacking sequences in the AlN polytypes.

The numerical calculations were performed using the HP xw4400, xw4600 workstations and the numerical materials simulator [SR11000(Hitachi) and Altix(SGI)] in NIMS.

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