Theoretical discovery of stable structures of group III-V monolayers: The materials for semiconductor devices

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Group III-V compounds are very important as the materials of semiconductor devices. Stable structures of the monolayers of group III-V binary compounds have been discovered by using first-principles calculations. The primitive unit cell of the discovered structures is a rectangle, which includes four group-III atoms and four group-V atoms. A group-III atom and its three nearest-neighbor group-V atoms are placed on the same plane; however, these connections are not the sp$^3$ hybridization. The bond angles around the group-V atoms are less than the bond angle of sp$^3$ hybridization. The discovered structure of GaP is an indirect transition semiconductor, while the discovered structures of GaAs, InP, and InAs are direct transition semiconductors. Therefore, the discovered structures of these compounds have the potential of the materials for semiconductor devices, for example, water splitting photocatalysts. The discovered structures may become the most stable structures of monolayers which consist of other materials. © 2015 AIP Publishing LLC.

Graphene is a monolayer which consists of carbon atoms$^1$. Graphene has the potential of the material for various devices. However, graphene cannot be applied to semiconductor devices because the energy gap of graphene is zero. If the monolayers which consist of other materials have the finite energy gaps, these monolayers have the great potential of the materials for semiconductor devices.

Graphene has a hexagonal planar (PL) structure (Fig. 1(a)); and silicene which is the monolayer of silicon atoms has a hexagonal buckled (BK) structure (Fig. 1(b)).$^2,3$ Although carbon and silicon belong to the same group-IV elements, graphene and silicene have different structures. The structures of monolayers are very important, because the structures influence the electronic and optical properties of the monolayers. Bulk group V compounds such as GaN, GaAs, InP, etc., are very important as the materials of semiconductor devices, especially optoelectronic devices. Therefore, we consider the most stable structures of the monolayers of group III-V binary compounds, which include B, Al, Ga, or In atoms as group-III elements, and N, P, or As atoms as group-V elements. Previous researches$^4$–$^8$ reported that the most stable structures of BN, BP, BaS, AlN, GaN, and InN monolayers were the PL structures like a graphene.

Zhuang et al.$^7$ reported that AIP and AIAs monolayers became tetragonal (TETRA) structures (Fig. 1(c)). Şahin et al.$^8$ reported that GaP, GaAs, InP, and InAs monolayers became the BK structures like silicene, while Tong et al.$^8$ reported that these monolayers became hexagonal zigzag (ZIG) structures (Fig. 1(d)) recently. However, it has been discovered$^9$ that the most stable structures of GaP, GaAs, InP, and InAs monolayers become unknown structures (Fig. 1(e)), which will be called hexagonal armchair (ARM) structures after the side view on yz-coordinates. Therefore, this paper reports these discovered stable structures in detail.

We discuss the most stable structures of monolayers of group III-V binary compounds based on the first-principle calculations. The structural relaxations and energy calculations are performed by using two different methods with high accuracy.

One method is a density functional theory (DFT) using a plane wave basis set. The projector augmented wave (PAW) potentials$^{10,11}$ and the generalized gradient approximation given by Perdew-Burke-Énzerhof (PBE)$^{12}$ are adopted in the same way as in previous works.$^5$–$^8$ The full Heyd-Scuseria-Énzerhof (HSE06) functionals$^{13,14}$ are not used because of long calculation time. Cutoff energies for the plane wave basis set are 500 eV for compounds including N atoms and 400 eV for other compounds. The k-point sampling uses Monkhorst-Pack scheme, which employs a $20 \times 19 \times 1$ mesh for the ARM structures, and a $32 \times 32 \times 1$ mesh for other structures. First, approximate structures are searched by the full relaxations. Next, the local minimum energies are searched by the cell shape conserving relaxations under the conditions that the z distance between layers of the supercells is fixed at 18 Å, and that each lattice constant is changed at 0.01 Å intervals. The convergence criteria of electronic self-consistent calculations and ionic relaxations are $10^{-6}$ and $10^{-5}$ eV, respectively. These calculations are performed by using VASP 5.3.3 package.$^{15,16}$

Another method is a DFT using a Gaussian type orbital (GTO) basis set under the periodic boundary conditions. This method does not need the super-cells and does not use pseudo-potential because of all-electron calculations. HSE06 functionals and 6–311G(d,p) basis set are adopted. InP and InAs cannot be calculated, because 6–311G(d,p) basis set can apply to elements only from hydrogen (H) to krypton (Kr) in the periodic table. About 2000 k-points are requested in a unit cell. The convergences of electronic self-consistent calculations are that the maximum and the root mean square (RMS) of the variations of the density matrix are less than...
10^{-5} and 10^{-7}, respectively, and that the variation of the total-energy is less than 10^{-5} Hartree. The convergences of ionic relaxations are that the maximum and RMS of force are less than 2 \times 10^{-6} and 10^{-6} Hartree/Bohr, respectively, and that the maximum and RMS of displacement are less than 6 \times 10^{-6} and 4 \times 10^{-6} Bohr, respectively. These calculations are performed by using Gaussian 09 package.\(^{17}\)

Calculations are performed about all binary compounds of B, Al, Ga, or In atoms as group-III elements, and N, P, or As atoms as group-V elements. First, we consider BN, BP, BAs, AlN, GaN, and InN. The BK, ZIG, and ARM structures of these compounds changed into the PL structures during the structural relaxations. Table I shows the total-energy differences per atom $\Delta E$ of the TETRA structures of these compounds. $\Delta E$ is defined as the difference from the total-energy per atom of the PL structure of the same compound calculated by the same calculation method. The smaller the $\Delta E$ is, the more stable the structure is. $\Delta E$ of the TETRA structures are positive; therefore, the most stable structures of BN, BP, BAs, AlN, GaN, and InN monolayers are the PL structures. These results agree with Şahin’s conclusion that “all III-V compounds containing first row elements B or N have planar stable structures,”\(^{4}\) and agree with other previous researches.\(^{5, 8}\)

Next, we consider AlP and AlAs. Table I shows $\Delta E$ of the BK, TETRA, ZIG, and ARM structures of these compounds. The TETRA structure of each compound have the smallest $\Delta E$ in all structures by either calculation method; therefore, the most stable structures of AlP and AlAs monolayers are the TETRA structures. These results also agree with previous researches.\(^{7, 8}\)

Finally, we consider GaP, GaAs, InP, and InAs. In Table I, the ARM structure of each compound have the smallest $\Delta E$ in all structures. Therefore, the most stable structures of GaP, GaAs, InP, and InAs monolayers are the ARM structures. In order to examine the dynamical stability of the ARM structures, phonon spectra were calculated by the finite displacement method in a plain wave basis set with PBE approximation. A 2 × 2 × 1 supercell is used, and the $z$ distance between layers is 14 Å. Cutoff energies are 320 eV,

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|}
\hline
Material & Structure & PBE & HSE06 \\
\hline
BN & TETRA & 1109 & NC\(^a\) \\
BP & TETRA & 406 & NC\(^a\) \\
BAs & TETRA & 219 & NC\(^a\) \\
AlN & TETRA & 73 & NC\(^a\) \\
GaN & TETRA & 416 & NC\(^a\) \\
InN & TETRA & 209 & \\
AlP & BK & PL\(^b\) & PL\(^b\) \\
 & TETRA & −213 & −147\(^c\) \\
 & ZIG & −56 & −26 \\
 & ARM & −61 & −34 \\
AlAs & BK & −14 & −6 \\
 & TETRA & −296 & −334\(^c\) \\
 & ZIG & TETRA\(^d\) & −92 \\
 & ARM & TETRA\(^d\) & −99 \\
GaP & BK & −13 & −2 \\
 & TETRA & 13 & NC\(^a\) \\
 & ZIG & −76 & −66 \\
 & ARM & −83 & −74 \\
GaAs & BK & −62 & −31 \\
 & TETRA & −142 & NC\(^a\) \\
 & ZIG & −154 & −129 \\
 & ARM & −157 & −135 \\
InP & BK & −24 & \\
 & TETRA & −4 & \\
 & ZIG & −102 & \\
 & ARM & −110 & \\
InAs & BK & −70 & \\
 & TETRA & −138 & \\
 & ZIG & −173 & \\
 & ARM & −179 & \\
\hline
\end{tabular}
\caption{Total-energy differences per atom $\Delta E$ of various structures of all compounds calculated with PBE approximation and with HSE06 functional.}
\end{table}

\(^{a}\)Non-convergence.
\(^{b}\)Changed into the PL structure.
\(^{c}\)Calculated by using 6-31g(d) basis set.
\(^{d}\)Changed into the TETRA structure.
and the k-point sampling employs a $10 \times 10 \times 1$ mesh. The calculations are performed by using Phonopy 1.8.4.1 package\textsuperscript{18} and VASP 5.3.3 package. The results are shown by black lines in Fig. 2. Acoustic phonons near $\Gamma$ points slightly have imaginary frequencies for all compounds. It is known that in phonon calculations, imaginary acoustic phonons appear near $\Gamma$ points by computational errors because the translational invariance is violated in approximated calculations. The main violation comes from the discreteness of the FFT-mesh.\textsuperscript{4} In order to examine the influence of the FFT-mesh, the additional phonon calculation of GaAs was performed by using a finer FFT-mesh that contains 8 times more points. In Fig. 2(b), to use finer FFT-mesh, the region formed by using a finer FFT-mesh that contains 8 times the region around the group-III atoms and the group-V atoms, respectively. Blue dashed lines indicate the bond angles of sp$^2$ and sp$^3$ hybridizations.

![FIG. 2. Phonon spectra of ARM structures. Red lines of GaAs are calculated by using a finer FFT-mesh. The inset is the first Brillouin zone of the ARM structure.](image)

![FIG. 3. (Lower panel) bond lengths and (upper panel) bond angles of ARM structures. Black and red were calculated with PBE approximation and with HSE06 functional, respectively. Triangles and pentagons are the bond angles around the group-III atoms and the group-V atoms, respectively. Blue dashed lines indicate the bond angles of sp$^2$ and sp$^3$ hybridizations.](image)

Now, we examine the characteristics of the ARM structures (Fig. 1(e)). The primitive unit cell of the ARM structure is a rectangle, which include four group-III atoms and four group-V atoms. These atoms are connected in honeycomb-like structure. The positions of atoms are expressed by seven structural parameters $T_x, T_y, x_3, y_3, z_3, y_5,$ and $z_5$ in Cartesian coordinates (Table II). The positions of group-III atoms are $(x_3, -y_3, z_3)$, $(x_3 + T_y/2, y_3, z_3)$, $(x_3, -y_3 + T_y/2, -z_3)$, and $(x_3 + T_y/2, y_3 + T_y/2, -z_3)$. The positions of group-V atoms are $(0, y_5, z_5)$, $(T_y/2, -y_5, z_5)$, $(0, y_5 + T_y/2, -z_5)$, and $(T_y/2, -y_5 + T_y/2, -z_5)$. Uneven monolayers like the ARM structure belong to the 80 crystallographic layer group types which are three-dimensional groups with two-dimensional translations. The ARM structure has no point group symmetries except the identity, and has two glide reflection and one screw rotation. In Fig. 1(e), the glide reflections are a reflection in x-z plane with glide vector $(T_y/2, 0, 0)$, and a reflection in x-y plane with glide vector $(0, T_y/2, 0)$. The screw rotation is a rotation of $180^\circ$ around the axis $y = T_y/4$, $z = 0$ with screw vector $(T_y/2, 0, 0)$. Therefore, the ARM structure belongs to layer group (pb21a).\textsuperscript{19} The ARM structure has three kinds of the bond lengths $(a, b, c)$; three kinds of the bond angles $(\alpha, \beta, \gamma)$ around the group-III atoms; and three kinds of the bond angles $(\phi, \theta, \psi)$ around the group-V atoms.

### TABLE II. Structural parameters, energy gaps $E_g$, and transition types of ARM structures calculated with PBE approximation and with HSE06 functional.

<table>
<thead>
<tr>
<th>Material</th>
<th>Method</th>
<th>$T_x$</th>
<th>$T_y$</th>
<th>$x_3$</th>
<th>$y_3$</th>
<th>$z_3$</th>
<th>$y_5$</th>
<th>$z_5$</th>
<th>$E_g$ (eV)</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaP</td>
<td>PBE</td>
<td>6.43</td>
<td>6.98</td>
<td>1.04</td>
<td>0.89</td>
<td>0.27</td>
<td>1.03</td>
<td>1.06</td>
<td>2.11</td>
<td>Indirect</td>
</tr>
<tr>
<td></td>
<td>HSE06</td>
<td>6.42</td>
<td>6.99</td>
<td>1.04</td>
<td>0.88</td>
<td>0.27</td>
<td>1.04</td>
<td>1.03</td>
<td>2.96</td>
<td>Indirect</td>
</tr>
<tr>
<td>GaAs</td>
<td>PBE</td>
<td>6.58</td>
<td>6.97</td>
<td>1.06</td>
<td>0.89</td>
<td>0.32</td>
<td>1.10</td>
<td>1.27</td>
<td>1.76</td>
<td>Direct</td>
</tr>
<tr>
<td></td>
<td>HSE06</td>
<td>6.58</td>
<td>7.03</td>
<td>1.05</td>
<td>0.89</td>
<td>0.32</td>
<td>1.10</td>
<td>1.22</td>
<td>2.56</td>
<td>Direct</td>
</tr>
<tr>
<td>InP</td>
<td>PBE</td>
<td>6.89</td>
<td>7.49</td>
<td>1.10</td>
<td>0.94</td>
<td>0.32</td>
<td>1.15</td>
<td>1.21</td>
<td>2.09</td>
<td>Direct</td>
</tr>
<tr>
<td>InAs</td>
<td>PBE</td>
<td>7.00</td>
<td>7.46</td>
<td>1.10</td>
<td>0.94</td>
<td>0.37</td>
<td>1.23</td>
<td>1.42</td>
<td>1.78</td>
<td>Direct</td>
</tr>
</tbody>
</table>
In Fig. 3, there are hardly any differences of the structures between the two calculation methods. The bond lengths of each compound are almost the same. Very interestingly, the relationship between the two calculation methods. The bond lengths of GaAs, InP, and InAs are more reliable than $E_g$ calculated with PBE approximation.

$E_{\text{red}}^{\text{H}_2/\text{H}_2^+} = -4.44 \text{ eV} + \text{pH} \cdot 0.059 \text{ eV}$. The oxidation potential is $E_{\text{OX}}^{\text{H}_2/\text{H}_2O} = -5.67 \text{ eV} + \text{pH} \cdot 0.059 \text{ eV}$.

In conclusion, the most stable structures of BN, BP, BAs, AlN, GaN, and InN monolayers are the PL structures; AIP and AlAs monolayers are the TETRA structures. However, GaP, GaAs, InP, and InAs monolayers become the discovered ARM structures. The BK structures and the ZIG structures are not the most stable structures of group III-V monolayers any longer. The ARM structure of GaP is an indirect transition semiconductor, while the ARM structures of GaAs, InP, and InAs are direct transition semiconductors. Therefore, the ARM structures of these compounds have the potential of the materials for semiconductor devices, for example, water splitting photocatalysts. The ARM structures may become the most stable structures of monolayers which consist of other materials.

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\[ See supplementary material at http://dx.doi.org/10.1063/1.4936553 for the process of the discovery of the ARM structure. \]
\[ M. J. Frisch et al., Gaussian 09, Revision C.01 (Gaussian, Inc., Wallingford CT, 2010). \]
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The process of the discovery of the ARM structure is explained briefly. When other group III-V materials were calculated, the author noticed that the group-III atoms preferred planar connections, and the group-V atoms preferred solid connections. The author thought that the bond angle $\theta_3$ around the group-III atoms of the BK structure might be different from the bond angle $\theta_5$ around the group-V atoms. Every other group-V atom in Fig. S1(a) was reflected in the plane where the group-III atoms existed. Then, the ZIG structure was obtained after the structural relaxation. The unit cell of the ZIG structure was doubled in y coordinate, and atoms within purple dashed rectangles in Fig. S1(b) were reflected in the x-y plane. Then, the ARM structure was obtained after the structural relaxation. The author searched other stable structures considering solid geometry about various unit cells, and discovered several metastable structures, for example, Fig. S2. The total-energy difference per atom $\Delta E$ of the metastable structure is smaller than the BK structure; however, $\Delta E$ is larger than the ZIG structure. Structure search algorithm did not be used.

FIG. S1. (a) Solid line is the x-z side view of BK structure. $\theta_3$ and $\theta_5$ are the bond angles around the group-III and group-V atoms, respectively. (b) The top view of ZIG structure. Green rectangle is the modified primitive unit cell.

FIG. S2. Other metastable structures of group III-V monolayers.