

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 firstprinciples 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 nearestneighbor group-V atoms are placed on the same plane; however, these connections are not the sp² hybridization. The bond angles around the group-V atoms are less than the bond angle of sp³ 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. [http://dx.doi.org/10.1063/1.4936553]

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 III-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 AlAs monolayers became tetragonal (TETRA) structures (Fig. 1(c)). Şahin et al.⁴ 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 discovered⁹ 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-Enzerhof (PBE)¹² are adopted in the same way as in previous works.⁶⁻⁸ The full Heyd-Scuseria-Ernzerhof (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 18Å, 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

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FIG. 1. The various structures of group III-V monolayers. The upper left is the top view on xy-coordinates. The lower left and upper right are the x-z and y-z side views, respectively. A green parallelogram is a primitive unit cell. Blue and red circles are group-III and group-V atoms, respectively. In order to understand the structures clearly, different marks are used according to the positions in the primitive unit cell, even if the atoms are the same element. a, b, and c are the bond lengths. α, β , and γ are the bond angles around the group-III atoms. ϕ , θ , and ψ are the bond angles around the group-V atoms. $T_x, T_y, x_3, y_3, z_3, y_5$, and z_5 are the structural parameters.

 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 2×10^{-6} and 10^{-6} Hartree/Bohr, respectively, and that the maximum and RMS of displacement are less than 6×10^{-6} and 4×10^{-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 totalenergy differences per atom ΔE of the TETRA structures of these compounds. ΔE 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 ΔE is, the more stable the structure is. ΔE 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 Sahin'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 ΔE of the BK, TETRA, ZIG, and ARM structures of these compounds. The TETRA structure of each compound have the smallest ΔE 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 has the smallest ΔE 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 $2 \times 2 \times 1$ supercell is used, and the z distance between layers is 14 Å. Cutoff energies are 320 eV,

TABLE I. Total-energy differences per atom ΔE of various structures of all compounds calculated with PBE approximation and with HSE06 functional.

		$\Delta E (meV/atom)$			
Material	Structure	PBE	HSE06		
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			

^aNon-convergence.

^bChanged into the PL structure.

^cCalculated by using 6-31g(d) basis set.

^dChanged into the TETRA structure.



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.

and the k-point sampling employs a $10 \times 10 \times 1$ mesh. The calculations are performed by using Phonopy 1.8.4.1 pack age^{18} and VASP 5.3.3 package. The results are shown by black lines in Fig. 2. Acoustic phonons near Γ points slightly have imaginary frequencies for all compounds. It is known that in phonon calculations, imaginary acoustic phonons appear near Γ points by computational errors because the translational invariance is violated in approximated calculations. The main violation comes from the discreteness of the FFT-mesh.⁴ In order to examine the influence of the FFTmesh, 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 of the imaginary phonon was narrowed. Hence, the imaginary phonons in Fig. 2 are the artifacts of the mesh size. All spectra of Fig. 2 have real frequencies; therefore, the dynamical stability of the ARM structures is confirmed.

Now, we examine the characteristics of the ARM structures (Fig. 1(e)). The primitive unit cell of the ARM structure



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.

is a rectangle, which include four group-III atoms and four group-V atoms. These atoms are connected in honeycomblike 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 $(x_3, -y_3, z_3), (x_3 + T_x/2, y_3, z_3), (x_3, -y_3 + T_y/2, -z_3),$ and $(x_3 + T_x/2, y_3 + T_y/2, -z_3)$. The positions of group-V atoms are $(0, y_5, z_5)$, $(T_x/2, -y_5, z_5)$, $(0, y_5 + T_y/2, -z_5)$, and $(T_x/2, -y_5 + T_y/2, -z_5)$. 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 $(T_x/2, 0, 0)$, and a reflection in x-y plane with glide vector $(0, T_y/2, 0)$. The screw rotation is a rotation of 180° around the axis $y = T_y/4$, z = 0 with screw vector $(T_x/2, 0, 0)$. Therefore, the ARM structure belongs to layer group $(pb2_1a)$.¹⁹ The ARM structure has three kinds of the bond lengths (a, b, c); three kinds of the bond angles (α, β, γ) around the group-III atoms; and three kinds of the bond angles (ϕ, θ, ψ) around the group-V atoms.

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

		Structural parameters (Å)								
Material	Method	T _x	T_y	x ₃	y ₃	Z ₃	У5	Z5	$E_{g}\left(eV\right)$	Transition
GaP	PBE	6.43	6.98	1.04	0.89	0.27	1.03	1.06	2.11	Indirect
	HSE06	6.42	6.99	1.04	0.88	0.27	1.04	1.03	2.96	Indirect
GaAs	PBE	6.58	6.97	1.06	0.89	0.32	1.10	1.27	1.76	Direct
	HSE06	6.58	7.03	1.05	0.89	0.32	1.10	1.22	2.56	Direct
InP	PBE	6.89	7.49	1.10	0.94	0.32	1.15	1.21	2.09	Direct
InAs	PBE	7.00	7.46	1.10	0.94	0.37	1.23	1.42	1.78	Direct



FIG. 4. Energy bands of ARM structures. Black and red were calculated with PBE approximation and with HSE06 functional, respectively. Blue and green lines indicate the redox potentials for water splitting at pH=0 and pH=7, respectively. The origin of energy is the vacuum level.

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 $\alpha + \beta + \gamma = 360^{\circ}$ holds. This relationship means that a group-III atom and its three nearest-neighbor group-V atoms are placed on the same plane. However, these connections are not the sp² hybridization, because the relationship $\alpha = \beta = \gamma = 120^{\circ}$ does not hold. On the other hand, the bond angles ϕ, θ, ψ around the group-V atom are less than $\cos^{-1}(-1/3) \approx 109.5^{\circ}$, which is the bond angle of sp³ hybridization.

Fig. 4 shows the energy bands of the ARM structures. GaP is an indirect transition semiconductor, while GaAs, InP, and InAs are direct transition semiconductors. In Table II, E_g calculated with PBE approximation is smaller than E_g calculated with HSE06 functional. It is well known that the PBE approximation in a plain wave basis set underestimate the energy gaps.²⁰ HSE03 functional¹³ in a Gaussian type orbital basis set produces good agreement with experimental energy gaps.²¹ Therefore, E_g calculated with HSE06 functional are more reliable than E_g calculated with PBE approximation.

Semiconductors can be used as water splitting photocatalysts if the conduction band minimum (CBm) energy is higher than the reduction potential for H^+/H_2 , and the valence band maximum (VBM) energy is lower than the oxidation potential for O_2/H_2O . The reduction potential is $E_{\rm H^+/H_2}^{red} = -4.44 \text{ eV} + \text{pH} \cdot 0.059 \text{ eV}$. The oxidation potential is $E_{\rm O_2/H_2O}^{ox} = -5.67 \text{ eV} + \text{pH} \cdot 0.059 \text{ eV}$.²² Fig. 4 shows the redox potentials at pH = 0 and pH = 7. The band edges of GaP and GaAs calculated with HSE06 functional straddle the redox potentials. The band edges of InP calculated with PBE approximation straddle the redox potentials at pH = 7. The band edges of InAs calculated with PBE approximation straddle the redox potentials by a narrow margin. However, the band edges of the real ARM structure of InAs probably straddle the redox potentials, because the PBE approximation underestimates the energy gaps. Therefore, the ARM structures of these compounds are the candidates of water splitting photocatalysts.

In conclusion, the most stable structures of BN, BP, BAs, AlN, GaN, and InN monolayers are the PL structures; AlP 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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APPLIED PHYSICS LETTERS 107, 213105 (2015) Supplementary Material

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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 θ_3 around the group-III atoms of the BK structure might be different from the bond angle θ_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, for example, Fig. S2. The total-energy difference per atom ΔE of the metastable structure is smaller than the BK structure; however, ΔE 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. θ_3 and θ_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.