Energetics and hydrogen passivation of carbon-related defects in InAs and $In_{0.5}Ga_{0.5}As$

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(Received 25 August 1995)

We perform *ab initio* pseudopotential calculations for studying the stability of carbon-related defects and the atomic model for the hydrogen passivation of substitutional carbons in InAs. Among various C-related defects, the most stable one is found to be a substitutional C acceptor occupying an As site. As compared to GaAs, substitutional C impurities are found to have higher formation energies, due to large lattice distortions surrounding the C atom, thus, C incorporation into bulk InAs is more difficult. Because of the small atomic radius and deep atomic energy levels of C, when C occupies an In site, its defect energy level lies below the valence band maximum (VBM), and it behaves as an acceptor, however, the formation energy is much higher than for C_{As}. We note that an inversion between the VBM and the C_{In} energy level takes place as pressure increases. For both the substitutional C_{As} and C_{In}, we find that hydrogen neutralizes the electrical activity of acceptors by occupying a bond-centered site between the C atom and one of its neighbors. In an $In_{0.5}Ga_{0.5}As$ alloy, the C acceptor is found to favor an As site with In neighbors, with the formation energy lying between InAs and GaAs. Thus, the calculated acceptor concentration of 10^{17} – 10^{18} cm^{-3} is much lower than the maximum carrier density achievable in GaAs.

I. INTRODUCTION

Carbon acceptors in GaAs and $Al_xGa_{1-x}As$ alloys have been known to have high doping efficiency, and lower diffusivity than other acceptors, such as Zn and Be.[1–4] In In-based materials, such as $In_xGa_{1-x}As$ and $In_xGa_{1-x}P$, however, it is more difficult to achieve high p-type doping levels with carbon impurities.[5–9] Kamp and his co-workers reported that $In_{0.5}Ga_{0.5}As$ layers grown with trimethyl indium (TMI) and trimethyl gallium are n-type with $n=5\times10^{17}$ cm^{-3}.[5] Based on their experiments, they suggested that C behaves as a donor in InAs, while it becomes an acceptor in GaAs, thus, the amphoteric behavior of C in $In_xGa_{1-x}As$ is expected, leading to a high degree of compensation. Similar behavior was also found by Abernathy and his co-workers, however, they suggested that p-type $In_xGa_{1-x}As$, with $p=1\times10^{19}$ cm^{-3}, could be achieved using an elemental In source instead of TMI.[10] Chin and his co-workers demonstrated that highly p-type $In_{0.5}Ga_{0.5}As$ epilayers can be grown, using CCl_4 as a doping source and found the highest hole concentration of $p=3\times10^{19}$ cm^{-3} after a post-growth anneal.[11] This result indicated that unintentional hydrogen passivation occurs during growth, and the post-growth anneal is necessary to obtain high hole concentrations.[11,12] However, the p-type doping level is far below the hole concentration of about 10^{21} cm^{-3} achievable with C acceptors in GaAs. Depending on carbon source and growing method, $In_xGa_{1-x}P$ films doped with C exhibit similar behavior, i.e., either weakly n-type or p-type.[8,9] Thus, the presence of In affects significantly the doping property of In-based semiconductors.

In this paper, we study the stability of C-related defects in InAs and $In_{0.5}Ga_{0.5}As$ alloy and compare the results with those for GaAs through first-principles pseudopotential calculations. Calculating the formation energies for various C-related defects, including native point defects and C-C complexes, we examine the energetics and find that C incorporation into bulk InAs is extremely difficult, as compared to GaAs. Among C-related defects, the C_{As} acceptor is found to be a dominant defect, however, this defect has a higher formation energy than an As-antisite or an In vacancy. In InAs, our results show that a substitutional C occupying an In site behaves as an acceptor with the energy level lying just below the valence band maximum. In an $In_{0.5}Ga_{0.5}As$ alloy, we also calculate the formation energies of substitutional C impurities, by employing a supercell containing a defect in the [001]-ordered double-layer superlattice, $(InAs)_2/(GaAs)_2$, and find that substitutional C impurities are more stable than in InAs. However, their formation energies are still higher than those in GaAs, leading to lower acceptor concentrations of about 10^{17} – 10^{18} cm^{-3}. For both substitutional C_{As} and C_{In} impurities in InAs, we find that hydrogen passivates their electrical activities by occupying a bond-centered site between C and one of its neighboring atoms rather than an antibonding site of C, similar to the H-C complexes in GaAs,[13] while the H atom at an antibonding site is directly bonded to the donor atom in Si.[14,15]

In Sec. II, we briefly describe the method of calculation. In Sec. III, the results of the calculations for C impurities in InAs and $In_{0.5}Ga_{0.5}As$ are presented and discussions are made. We summarize the results in Sec. IV.

II. METHOD

The stability of a defect in binary compound is determined by calculating the formation energy defined as in Ref. 16,

$$\Omega_D=E_D+Q_D\mu_e-n_{In}\mu_{In}-n_{As}\mu_{As}-n_C\mu_C \quad (1)$$

$$=E'_D+Q_D\mu_e-\frac{1}{2}(n_{In}-n_{As})\Delta\mu-n_C(\mu_C-\mu_C^B), \quad (2)$$

where E_D is the total energy of a supercell containing the defect in a charge state Q_D, μ_e is the electron chemical potential relative to the bulk valence band maximum, and n_i's and μ_i's ($i=$ In, As, and C) are the numbers and the

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chemical potentials of constituents in the supercell, respectively. The superscript B denotes the corresponding bulk value. The defect energy E'_D in Eq. (2) is written in the form

$$E'_D=E_D-\frac{1}{2}(n_{\mathrm{In}}+n_{\mathrm{As}})\mu_{\mathrm{InAs}}-\frac{1}{2}(n_{\mathrm{In}}-n_{\mathrm{As}})(\mu^B_{\mathrm{In}}-\mu^B_{\mathrm{As}})-n_{\mathrm{C}}\mu^B_{\mathrm{C}}, \tag{3}$$

and the chemical potential difference is defined as $\Delta\mu=(\mu_{\mathrm{In}}-\mu_{\mathrm{As}})-(\mu^B_{\mathrm{In}}-\mu^B_{\mathrm{As}})$. The chemical potential of In (As) does not exceed that of bulk In (As), otherwise, bulk In (As) would be formed. In addition, the sum of the chemical potentials, μ_{In} and μ_{As}, is equal to the chemical potential of bulk InAs, i.e., $\mu_{\mathrm{In}}+\mu_{\mathrm{As}}=\mu_{\mathrm{InAs}}$, because the exchange of an In-As pair between the reservoir and bulk InAs takes place in thermal equilibrium. Then, the chemical potentials are restricted by the constraints, $0<\mu_e<E_g$, $\mu_{\mathrm{C}}<\mu^B_{\mathrm{C}}$, and $-\Delta H\leqslant\Delta\mu\leqslant\Delta H$, where ΔH is the heat of formation of bulk InAs, and its value is calculated to be 0.93 eV per pair, which is higher than the measured value of 0.60 eV.[17] The energy band gap (E_g) is calculated to be 0.52 eV, while the measured value is 0.42 eV.[18] When μ_{In} (μ_{As}) reaches its maximum value μ^B_{In} (μ^B_{As}), i.e., the In(As)-rich limit, $\Delta\mu$ has an extremum value of ΔH ($-\Delta H$). Extending the formula for Ω_D to ternary semiconductor alloys is straightforward, as given in the Appendix.

The calculations are based on the first-principles pseudopotential method[19] within the local-density-functional approximation .[20] The Wigner interpolation formula is used for the exchange and correlation potential.[21] Norm-conserving nonlocal pseudopotentials are generated by the scheme of Troullier and Martins and transformed into the separable form of Kleinman and Bylander.[22] We employ a supercell containing 32 atoms, which forms a bcc structure for defects in InAs. In the case of $\mathrm{In_{0.5}Ga_{0.5}As}$, we model the alloy system by a two-layer $(\mathrm{InAs})_2/(\mathrm{GaAs})_2$ superlattice stacked along the [001] direction, then use a 32-atom tetragonal supercell containing a defect. The wave functions are expanded in a plane-wave basis set, with a kinetic energy cutoff of 25 Ry throughout this work. To perform the Brillouin zone summation of the charge density, we use two special **k** points, $2\pi/a$ (1/8, 1/8, 1/8) and (3/8, 3/8, 3/8), in the irreducible sector of the bcc supercell Brillouin zone, while one **k** point $2\pi/a$ (0, 1/2, 1/4), for a tetragonal supercell, where a is the lattice constant is used. Increasing the kinetic energy cutoff and the number of **k** points, we find the maximum error in estimating relative formation energies to be less than 0.2 eV per C atom in a supercell, which is much smaller than the formation energies calculated for defects considered here. The energy functional is fully minimized by the modified-Jacobi relaxation method, which was recently developed and employed successfully for a variety of systems.[23] We relax internal ionic positions by calculating the Hellmann-Feynman forces[24] until the optimized atomic configuration is obtained.

III. RESULTS

A. Stability of defects in InAs

In InAs, we examine the stability of various defects including substitutionals ($\mathrm{C_{As}}$ and $\mathrm{C_{In}}$), vacancies ($\mathrm{V_{As}}$ and $\mathrm{V_{In}}$), antisites ($\mathrm{As_{In}}$ and $\mathrm{In_{As}}$), an interstitial C, a [100]-split interstitial C-C complex, and substitutional-antisite complexes ($\mathrm{C_{As}}$-$\mathrm{As_{In}}$ and $\mathrm{C_{In}}$-$\mathrm{In_{As}}$). The calculated formation energies (Ω_D) for major defects are presented in Table I and are plotted as a function of carbon chemical potential for both As- and In-rich conditions in Figs. 1 and 2. In As-rich conditions (see Fig. 1), an As-antisite ($\mathrm{As_{In}}^{2+}$) is found to be most stable in p-type InAs, while in n-type materials, an In vacancy ($\mathrm{V_{In}}^{3-}$) is lowest in energy. Among C-related defects, we find that the C atom has the minimum energy when located at an As site, behaving as an acceptor, however, this defect is less stable than native defects, such as $\mathrm{As_{In}}^{2+}$, $\mathrm{As_{In}}^{0}$, and $\mathrm{V_{In}}^{3-}$ over a wide range of the C chemical potential. As μ_{C} increases, the difference of the formation energies between the $\mathrm{C_{As}}^-$ acceptor and the $\mathrm{As_{In}}^{2+}$ antisite decreases rapidly and reaches about 1.5 eV at the maximum value of μ_{C} in p-type InAs, while the formation energy of $\mathrm{C_{As}}^-$ is higher by about 0.9 eV than for $\mathrm{V_{In}}^{3-}$ at $\mu_{\mathrm{C}}=\mu^B_{\mathrm{C}}$ in n-type InAs. In In-rich conditions (see Fig. 2), an In-antisite ($\mathrm{In_{As}}$) has the lowest formation energy for lower carbon chemical potentials in both p- and n-type InAs. In contrast to the As-rich condition, the formation energy of the $\mathrm{C_{As}}^-$ acceptor becomes comparable to that for an In-antisite, especially, near the maximum C chemical potential. The dominant defects in As-rich conditions are found to be $\mathrm{As_{In}}$ and $\mathrm{V_{In}}$, as expected from the fact that the amount of In is relatively lower in the As-rich limit, while $\mathrm{In_{As}}$ and $\mathrm{C_{As}}$ are more stable than any other defects in In-rich conditions. For an interstitial C, we test tetrahedral interstitial positions, which are surrounded by either In or As atoms, and find both sites to have higher formation energies (E'_D = 5.6 – 6.5 eV).

In GaAs, the dominant defects at very high doping levels were shown to be [100] split-interstitial $(\mathrm{C}\text{-}\mathrm{C})_{[100]}$ com-

TABLE I. Contributions to the formation energy Ω_D are listed for the C-related and native defects in InAs for various charge states. Details of μ_e, μ_{C}, and $\Delta\mu$ are discussed in the text.

Defect	E'_D(eV)	$+Q_D\mu_e$	$-\frac{1}{2}(n_{\mathrm{In}}-n_{\mathrm{As}})\Delta\mu$	$-n_{\mathrm{C}}(\mu_{\mathrm{C}}-\mu^B_{\mathrm{C}})$
$\mathrm{As_{In}}^0$	3.03		$+\Delta\mu$	
$\mathrm{As_{In}}^{2+}$	2.61	$+2\mu_e$	$+\Delta\mu$	
$\mathrm{In_{As}}^0$	3.26		$-\Delta\mu$	
$\mathrm{In_{As}}^{2-}$	3.67	$-2\mu_e$	$-\Delta\mu$	
$\mathrm{V_{As}}^0$	3.75		$-\frac{1}{2}\Delta\mu$	
$\mathrm{V_{As}}^-$	4.15	$-\mu_e$	$-\frac{1}{2}\Delta\mu$	
$\mathrm{V_{As}}^+$	3.33	$+\mu_e$	$-\frac{1}{2}\Delta\mu$	
$\mathrm{V_{In}}^0$	4.86		$+\frac{1}{2}\Delta\mu$	
$\mathrm{V_{In}}^+$	5.55	$+\mu_e$	$+\frac{1}{2}\Delta\mu$	
$\mathrm{V_{In}}^-$	4.16	$-\mu_e$	$+\frac{1}{2}\Delta\mu$	
$\mathrm{V_{In}}^-$	3.62	$-3\mu_e$	$+\frac{1}{2}\Delta\mu$	
$\mathrm{C_{As}}^0$	3.28		$-\frac{1}{2}\Delta\mu$	$-(\mu_{\mathrm{C}}-\mu^B_{\mathrm{C}})$
$\mathrm{C_{As}}^-$	2.80	$-\mu_e$	$-\frac{1}{2}\Delta\mu$	$-(\mu_{\mathrm{C}}-\mu^B_{\mathrm{C}})$
$\mathrm{C_{In}}^0$	5.48		$+\frac{1}{2}\Delta\mu$	$-(\mu_{\mathrm{C}}-\mu^B_{\mathrm{C}})$
$\mathrm{C_{In}}^+$	5.10	$+\mu_e$	$+\frac{1}{2}\Delta\mu$	$-(\mu_{\mathrm{C}}-\mu^B_{\mathrm{C}})$
$\mathrm{C_{In}}^-$	5.93	$-\mu_e$	$+\frac{1}{2}\Delta\mu$	$-(\mu_{\mathrm{C}}-\mu^B_{\mathrm{C}})$
$(\mathrm{CC})_{[100]}{}^0$	4.30		$-\frac{1}{2}\Delta\mu$	$-2(\mu_{\mathrm{C}}-\mu^B_{\mathrm{C}})$
$(\mathrm{CC})_{[100]}{}^+$	3.43	$+\mu_e$	$-\frac{1}{2}\Delta\mu$	$-2(\mu_{\mathrm{C}}-\mu^B_{\mathrm{C}})$
$(\mathrm{C_{As}}\text{-}\mathrm{As_{In}})^+$	4.76	$+\mu_e$	$+\frac{1}{2}\Delta\mu$	$-(\mu_{\mathrm{C}}-\mu^B_{\mathrm{C}})$
$(\mathrm{C_{In}}\text{-}\mathrm{In_{As}})^-$	6.19	$-\mu_e$	$-\frac{1}{2}\Delta\mu$	$-(\mu_{\mathrm{C}}-\mu^B_{\mathrm{C}})$

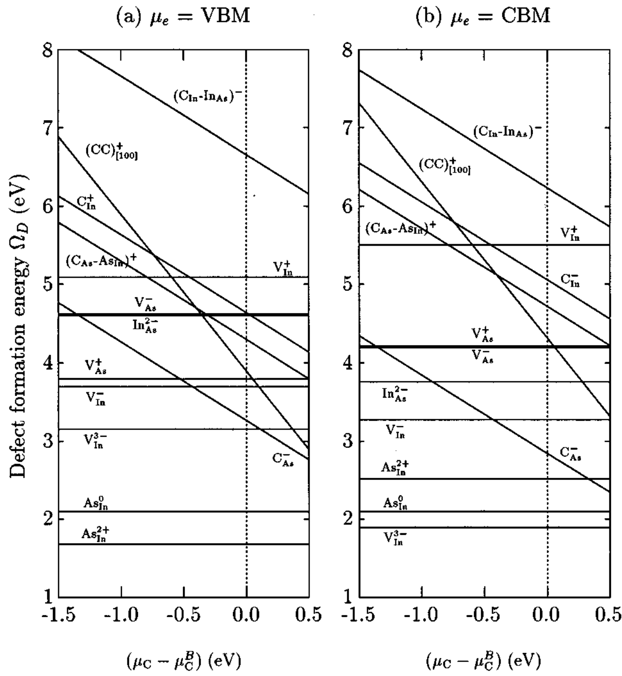

FIG. 1. The defect formation energies (Ω_D) for As-rich conditions are plotted as a function of the carbon chemical potential in (a) p-type ($\mu_e=0$) and (b) n-type ($\mu_e=E_g$) InAs.

plexes at As sites, which cause the compensation of C_{As} acceptors.[25] In InAs, however, the role of the C-C complex is found to be negligible, because of the high formation energy. Since a split-interstitial C-C pair involves two C atoms, its formation energy decreases twice as rapidly with the C

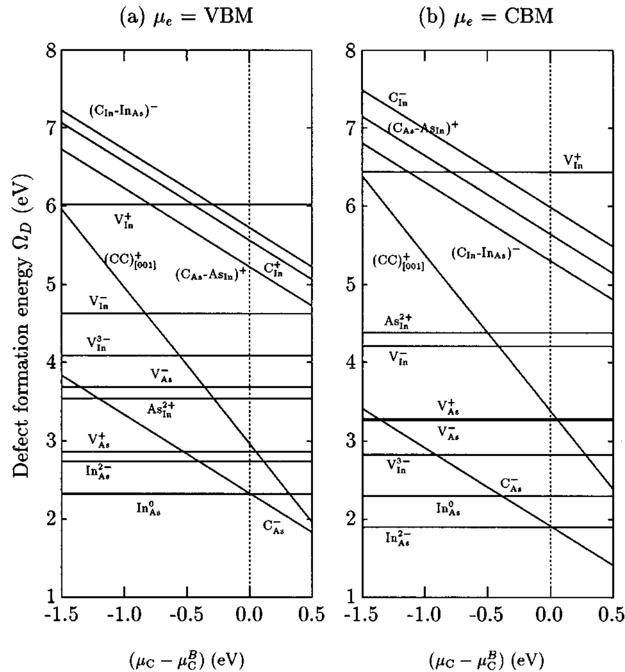

FIG. 2. The defect formation energies (Ω_D) for In-rich conditions are plotted as a function of the carbon chemical potential in (a) p-type ($\mu_e=0$) and (b) n-type ($\mu_e=E_g$) InAs.

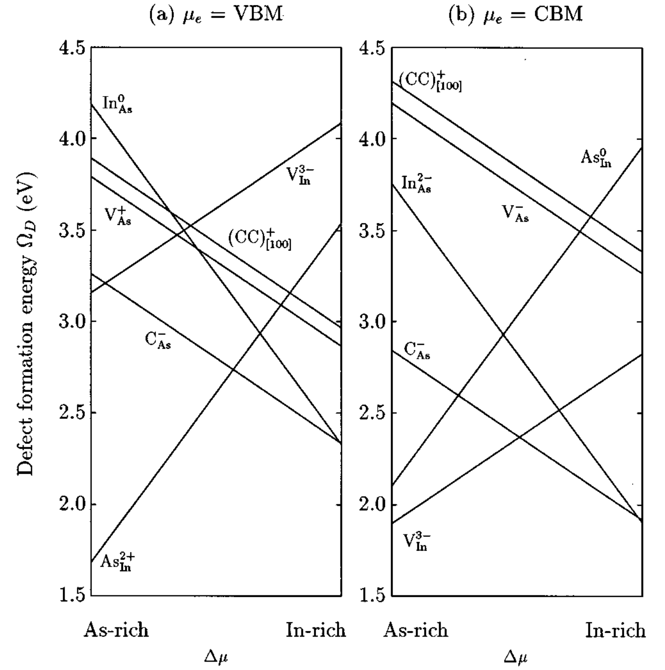

FIG. 3. The defect formation energies (Ω_D) at the maximum carbon chemical potential are plotted as a function of $\Delta\mu$ in (a) p-type ($\mu_e=0$) and (b) n-type ($\mu_e=E_g$) InAs.

chemical potential than for the C_{As}^- acceptor. Nevertheless, the formation energy of a $(C\text{-}C)_{[100]}^+$ complex is still higher by 0.63 eV than for C_{As}^- at $\mu_C=\mu_C^B$ in p-type InAs. In Fig. 3, the formation energies for various dominant defects are plotted as a function of $\Delta\mu$ for both p- and n-type InAs. In p-type InAs grown under As-rich conditions, the As-antisites are found to compensate for the C_{As} acceptors, resulting in extremely low p-doping levels. However, as going to the In-rich limit, since As_{In}^{2+} becomes less stable than C_{As}^-, the p-type doping level increases. Similar stability of the C_{As}^- acceptor is also found under In-rich conditions in n-type InAs. Thus, in In-rich conditions, C behaves predominantly as an acceptor at an As site, in good agreement with the experimental finding that, as the V/III flux ratio decreases, the hole concentration increases.[10]

For the substitutional C_{As}^- and C_{In}^- impurities, their four nearest neighbor atoms undergo large lattice relaxations of about 0.40 and 0.41 Å, respectively, toward the C atom, while lattice distortions for C_{As}^- and C_{Ga}^+ in GaAs were found to be 0.38 and 0.32 Å, respectively. In this case, although the trigonal C_{3v} symmetry is imposed by letting one of the impurity neighboring bonds be relaxed, symmetry-lowering distortions are not found. Because of the small atomic radius of the C atom, lattice distortions induced by substitutional C impurities are more significant than for vacancies and antisites, resulting in the 15–16 % reduction of the bond lengths. We find that both In and As vacancies also exhibit large lattice distortions, while the atomic relaxations surrounding the In- and As-antisites are smaller, as shown in Table II. Thus, antisites are generally more stable than vacancies, similar to GaAs. For antisites, slight symmetry-breaking relaxations from the tetrahedral symmetry might be an artifact of calculations caused by the use of supercells and a limited number of **k** points, while vacancies exhibit clearly

TABLE II. Atomic relaxations (in units of Å) of the defect nearest neighbors are compared. For each defect, $d_{[111]}$ and d_{off} denote distortions for the [111] neighbor and the remaining three nearest atoms, respectively. Positive (negative) values indicate outward (inward) relaxations from (toward) defects.

Defect	$d_{[111]}$	d_{off}	Defect	$d_{[111]}$	d_{off}
As_{In}^{2+}	-0.12	-0.11	In_{As}^{0}	0.03	0.14
As_{In}^{0}	-0.02	0.01	In_{As}^{2-}	0.03	0.02
V_{In}^{+}	-0.34	0.13	V_{As}^{+}	-0.07	-0.04
V_{In}^{0}	-0.26	0.00	V_{As}^{0}	-0.20	-0.09
V_{In}^{-}	-0.35	-0.16	V_{As}^{-}	-0.40	-0.22
V_{In}^{3-}	-0.25	-0.21			

the trigonal C_{3v} symmetry under full relaxations. We also test the D_{2h}-symmetry configuration for vacancies and find that their energies are higher by about 0.1 eV than for the C_{3v}-symmetry configuration.

In Fig. 4, the energy levels associated with s and p orbitals are compared for the C, As, In, and Ga atoms. Both the s and p orbital energies of the C and As atoms are much lower than those for the In and Ga atoms. For the C_{As}^{-} acceptor, since the C and As atoms have similar s- and p-atomic energies, their bonding s and p state energies between the C and its neighboring In atoms are similar to the bulk valence band of InAs, with the effective masslike acceptor level above the valence band maximum (VBM). In addition, since the In s orbital energy is higher than that of the Ga atom, the C_{As} atom in InAs is less strongly bonded to its neighboring In atoms, thus, the formation energy of the C_{As}^{-} acceptor is relatively higher, as compared to GaAs.[25] In the case of C_{In}^{-}, the C atom is directly bonded to the As atoms, which have much lower s- and p-orbital energies than for the In atom. Thus, the bonding s and p state energies lie deeper in the valence band than for C_{As}^{-}. However, since the antibonding s state lies at about 0.1 eV below the VBM, the substitutional C_{In} behaves as an acceptor, with the hole state at the VBM of the supercell. The hole densities associated with C_{In}^{0} spread out among first neighbor and more distant As atoms with a small distribution on C, while a large suppression of density occurs near the In atoms.

Although the existence of C_{In} in InAs is unlikely because of its high formation energy, it is interesting to see how the C-related energy level in the valence band varies with pressure. We find that the inversion between the C-related level

C	As	In	Ga
		p −2.89	p −2.88
p −5.42	p −5.42		
		s −7.97	s −8.98
s −13.59	s −14.23		

FIG. 4. The atomic energy levels of the C, As, In, and Ga atoms.

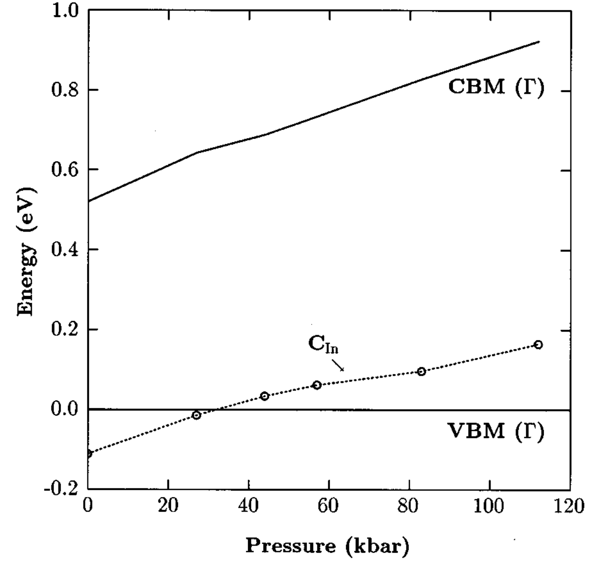

FIG. 5. The pressure variation of the defect energy level associated with C_{In} is drawn with respect to the valence band maximum.

and the VBM takes place at a pressure of about 30 kbar, as shown in Fig. 5. This result is similar to the stabilization of deep donor levels (DX centers) found in GaAs and $Al_xGa_{1-x}As$ alloys by applying pressure or increasing Al concentration, where the conduction band minimum and the DX level are interchanged.[26,27] In GaAs, the pressure variation of the shallow donor state follows the conduction band minimum, because it is an effective masslike level. Similar to the localized DX center, since the C_{In} defect level is induced by large lattice distortions of the donor neighboring atoms, the pressure variation of this defect level does not follow the VBM. Because of the small atomic radius of C, the effect of volume variation is more significant for the C-As bond than for the bulk In-As bond. As pressure increases, the C-As bond length reaches their covalent radii, and the C_{In}-related defect level rises above the VBM. Then, the C_{In} defect at high pressures behaves like a donor, i.e., the C_{Ga} donor level in GaAs is located above the VBM.[25]

B. Substitutional C impurities in $In_{0.5}Ga_{0.5}As$

Compared with the previous results for GaAs,[25] we find that the formation energy of C_{As} in InAs is higher by 1.8 eV, while, for C_{In}, it is much higher by 3.7 eV than for C_{Ga} in GaAs. Based on the calculated formation energies, the hole carrier concentration in InAs is estimated to be an order of 10^{12} cm^{-3}, which is much lower than the maximum hole density of 10^{21} cm^{-3} achievable in GaAs. Thus, in $In_xGa_{1-x}As$ alloys, C incorporation seems to be less effective in the presence of In. In fact, experiments showed that it is more difficult to achieve high p-type doping levels in $In_{0.5}Ga_{0.5}As$ alloys than in GaAs.[11]

To test the stability of substitutional C impurities in $In_{0.5}Ga_{0.5}As$, we calculate the defect formation energies for ternary semiconductor alloys (given in the Appendix). Here, we employ the [001]-ordered $(InAs)_2/(GaAs)_2$ superlattice to simulate the $In_{0.5}Ga_{0.5}As$ alloy, thus, we are able to see

TABLE III. Contributions to the formation energy Ω_D are listed for the substitutional C defects in $In_{0.5}Ga_{0.5}As$. Details of $\Delta\bar{\mu}$ and $\delta\bar{\mu}$ are discussed in the text. For C_{As1} and C_{As3}, the C atom is surrounded only by the Ga and In atoms, respectively, while C_{As2} has two Ga and two In neighbors.

Defect	E'_D(eV)	$+Q_D\mu_e$	$-\frac{1}{4}(n_{In}+n_{Ga}-n_{As})\Delta\bar{\mu}$	$-\frac{1}{2}(n_{In}-n_{Ga})\delta\bar{\mu}$	$-n_C(\mu_C-\mu_C^B)$
C_{Ga}^+	3.74	$+\mu_e$	$+\frac{1}{4}\Delta\bar{\mu}$	$-\frac{1}{2}\delta\bar{\mu}$	$-(\mu_C-\mu_C^B)$
C_{In}^+	3.93	$+\mu_e$	$+\frac{1}{4}\Delta\bar{\mu}$	$\frac{1}{2}\delta\bar{\mu}$	$-(\mu_C-\mu_C^B)$
C_{In}^-	5.33	$-\mu_e$	$+\frac{1}{4}\Delta\bar{\mu}$	$\frac{1}{2}\delta\bar{\mu}$	$-(\mu_C-\mu_C^B)$
C_{As1}^-	2.57	$-\mu_e$	$-\frac{1}{4}\Delta\bar{\mu}$	0	$-(\mu_C-\mu_C^B)$
C_{As2}^-	2.42	$-\mu_e$	$-\frac{1}{4}\Delta\bar{\mu}$	0	$-(\mu_C-\mu_C^B)$
C_{As3}^-	2.28	$-\mu_e$	$-\frac{1}{4}\Delta\bar{\mu}$	0	$-(\mu_C-\mu_C^B)$

the doping properties in this system. The calculated formation energies for C impurities at various substitutional sites are listed in Table III and are plotted at the maximum C chemical potential in As-, In-, and Ga-rich limits in Fig. 6. At an As site, the C atom has three different configurations, depending on the number of the Ga and In atoms in the first neighborhood; C_{As1} and C_{As3} are surrounded only by the Ga and In atoms, respectively, while C_{As2} has the equal numbers of the Ga and In neighbors. In this case, the most stable one is found to be C_{As3}, indicating that the C impurity in $In_{0.5}Ga_{0.5}As$ favors the In neighbors. In general, the C_{As}^- acceptor is more stable than for both C_{In} and C_{Ga}, and this behavior is more prominent in n-type materials. In InAs, we have shown that the effect of C_{In} on the doping property is almost negligible, however, this defect behaves as a donor in alloys. In p-type $In_{0.5}Ga_{0.5}As$, there are two regions where either the C_{In}^+ or C_{Ga}^+ donors compensate for the acceptors, i.e., the cation-rich (either Ga or In) limits under As-rich conditions. We find that the formation energies of substitutional C impurities in the $In_{0.5}Ga_{0.5}As$ alloy have roughly intermediate values between InAs and GaAs, leading to the acceptor concentrations of about $10^{17}-10^{18}$ cm^{-3}, which is lower by an order of magnitude than the measured maximum carrier density achieved with C impurities. Recent experiments showed that it is possible to obtain the p-type doping level of 3×10^{19} cm^{-3} after a post-growth anneal in CCl_4-doped $In_{0.5}Ga_{0.5}As$.[11] Since unintentional hydrogen passivation of C through the formation of H-C pairs is present in as-grown samples, the post-growth anneal is necessary to obtain high hole concentrations.[11,12] Thus, it is difficult to compare directly our calculated hole concentrations with experiments, where H plays an important role in the activation mechanism. We also point out that some alloys grown with trimethyl indium and trimethyl gallium exhibited n-type carriers.[5] Based on our results, we may expect that a type conversion from p-type to n-type is attributed to the formation of either As antisites or C donors at cation sites, not to As vacancies. In this case, the chemical reaction effect, which cannot be considered in our calculations, is certainly important in reaching thermal equilibrium of defects.

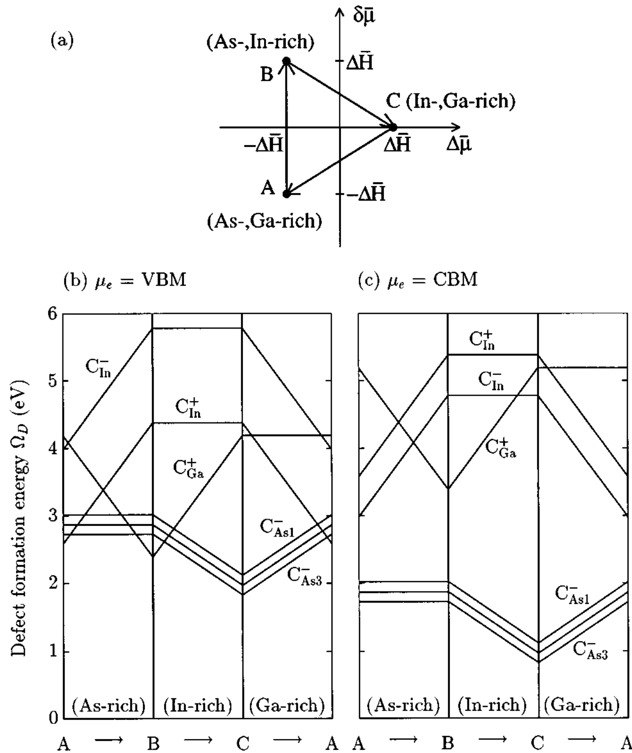

FIG. 6. (a) The As- $(A\rightarrow B)$, In- $(B\rightarrow C)$, and Ga-rich $(C\rightarrow A)$ conditions are drawn in the parameter space of $\Delta\bar{\mu}$ and $\delta\bar{\mu}$, which vary over the range bounded by the triangle. (b) The defect formation energies (Ω_D) at the maximum carbon chemical potential are plotted in the As-, In-, and Ga-rich limits in (a) p-type $(\mu_e=0)$ and (b) n-type $(\mu_e=E_g)$ $In_{0.5}Ga_{0.5}As$.

C. Hydrogen passivation of C in InAs

Finally, we examine the passivation of substitutional C impurities by hydrogen atoms in InAs. When atomic hydrogen is incorporated into GaAs and $In_xGa_{1-x}As$, a sizable amount of C impurities were found to form H-C complexes.[11,12,28] For both the substitutional C_{As} and C_{In} in InAs, we test various atomic models for the H passivation and find that hydrogen favors energetically a bond-center (BC) site between the C and its neighboring atoms rather than an antibonding (AB) site (see Fig. 7). Similar results were also reported for substitutional C atoms in GaAs.[13] In semiconductors, it is generally known that H is positioned at a BC site to passivate a shallow acceptor level, while for a donor-H complex H favors an AB site of the donor impurity.[14,15,29] For the C_{As} acceptor, the energy of the BC site is found to be lower by 0.38 eV than for the AB site. Then, H is strongly bonded to the acceptor with the bond length of 1.18 Å, and the bond angles between the C and its neighboring In atoms are reduced to 103.2° from its ideal value. For H at an AB site, the C acceptor is slightly shifted by 0.10 Å from its ideal position toward the AB site, maintaining the strong bonding between the C and H atoms with the bond length of 1.17 Å. In the case of C_{In}, since its defect energy level lies in the valence band, the H passivation is somewhat different from those usually found for shallow donors in Si and GaAs. For a Si donor in GaAs, H was shown to be positioned at an AB site and to weaken one of the Si-As bonds, with the Si donor displaced into the AB position.[29] As in the case of the H-C_{As} complex, the BC site is energetically more favorable by 0.35 eV than the AB position of

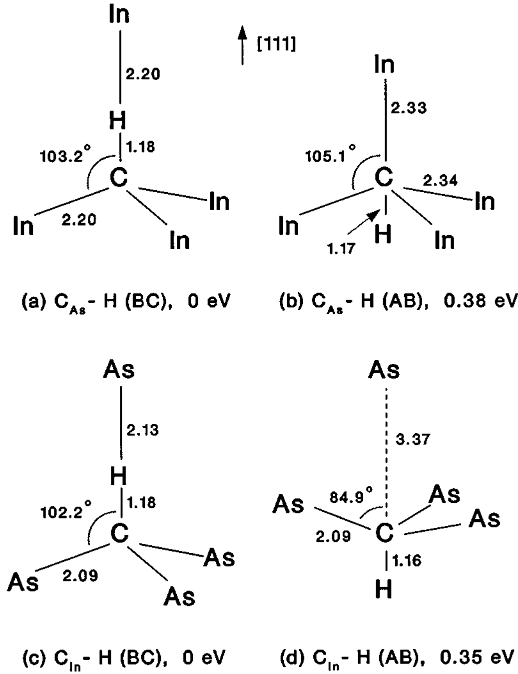

FIG. 7. Atomic configurations are drawn for the H-C_{As} and H-C_{In} complexes with the bond lengths in units of Å. For each substitutional C, the energy of the antibonding configuration is compared with that of the bond-centered-site configuration.

C_{In}, with a similar bond length of 1.18 Å for the H-C pair. This bond-centered configuration was also found for a H-C_{Ga} complex in GaAs.[13] This bond length is larger than the sum of two atomic radii, 0.32 Å for H and 0.77 Å for C.[30] For H at the AB site of C_{In}, the H-C bond is found to be so strong that the C atom is relaxed toward the H atom by 0.95 Å, lying far below the plane generated by the three neighboring As atoms (see Fig. 7). Thus, the bond between the C and [111] As atoms is nearly broken with the bond length of 3.37 Å, and the bond angles between the C and three neighboring As atoms are significantly reduced to 84.9°.

IV. SUMMARY

We have found that C-related defects in InAs are less stable than native point defects, such as As_{In}, In_{As}, and V_{In}. Because of the small size of the C atom, the C substitutionals induce large lattice distortions around the C atom, resulting in high formation energies. Thus, C incorporation into $In_{1-x}Ga_xAs$, with high In concentrations, is less effective than into GaAs. For both C_{As} and C_{In}, we find that H favors the bond-centered site between the C and its neighboring atoms rather than the antibonding site. The unusual atomic model for the hydrogen passivation of C_{In} results from the acceptor behavior of this defect, which has the defect level in the valence band. With increasing of pressure, the C_{In}-associated defect level is found to rise above the valence band maximum. In the $In_{0.5}Ga_{0.5}As$ alloy, the C atom at an anion site is found to favor a site with In neighbors, and the acceptor concentration is estimated to be about $10^{17}-10^{18}\ \mathrm{cm}^{-3}$, which is lower by an order of magnitude than the measured highest hole concentration. This result demonstrates that hydrogen passivation of C impurities plays an important role in achieving high carrier densities.

ACKNOWLEDGMENTS

This work was supported by the Ministry of Science and Technology, the CMS at KAIST, and the SPRC at Jeonbuk National University.

APPENDIX A: DEFECT FORMATION ENERGY FOR TERNARY ALLOYS

The defect formation energy for ternary semiconductor alloys is obtained in a similar way to Eqs. (2) and (3). In an $In_{0.5}Ga_{0.5}As$ alloy, the formation energy Ω_D of a defect in a supercell is written as

$$\Omega_D = E_D + Q_D\mu_e - n_{\mathrm{In}}\mu_{\mathrm{In}} - n_{\mathrm{Ga}}\mu_{\mathrm{Ga}} - n_{\mathrm{As}}\mu_{\mathrm{As}} - n_{\mathrm{C}}\mu_{\mathrm{C}}. \quad \text{(A1)}$$

The chemical potentials of constituents (μ_{In}, μ_{Ga}, and μ_{As}) are smaller than their corresponding bulk values, and satisfy the conditions of $\mu_{\mathrm{In}}+\mu_{\mathrm{As}}\leq\mu_{\mathrm{InAs}}$ and $\mu_{\mathrm{Ga}}+\mu_{\mathrm{As}}\leq\mu_{\mathrm{GaAs}}$. In thermal equilibrium, the sum of the chemical potentials is equal to the chemical potential of the alloy, i.e., $\mu_{\mathrm{In}}+\mu_{\mathrm{Ga}}+2\mu_{\mathrm{As}}=\mu_{\mathrm{InGaAs}_2}$. These conditions limit the ranges over which the chemical potentials can vary. Defining two parameters $\Delta\bar{\mu}$ and $\delta\bar{\mu}$,

$$\Delta\bar{\mu} = (\mu_{\mathrm{In}}+\mu_{\mathrm{Ga}}-2\mu_{\mathrm{As}}) - (\mu_{\mathrm{In}}^B+\mu_{\mathrm{Ga}}^B-2\mu_{\mathrm{As}}^B) \quad \text{(A2)}$$

and

$$\delta\bar{\mu} = (\mu_{\mathrm{In}}-\mu_{\mathrm{Ga}}) - (\mu_{\mathrm{In}}^B-\mu_{\mathrm{Ga}}^B), \quad \text{(A3)}$$

the formation energy in Eq. (A1) is rewritten as

$$\Omega_D = E_D' + Q_D\mu_e - \frac{1}{4}(n_{\mathrm{In}}+n_{\mathrm{Ga}}-n_{\mathrm{As}})\Delta\bar{\mu} - \frac{1}{2}(n_{\mathrm{In}}-n_{\mathrm{Ga}})\delta\bar{\mu} - n_{\mathrm{C}}(\mu_{\mathrm{C}}-\mu_{\mathrm{C}}^B), \quad \text{(A4)}$$

where

$$E_D' = E_D - \frac{1}{2}\left(n_{\mathrm{In}} - \frac{n_{\mathrm{As}}}{2}\right)(\mu_{\mathrm{In}}^B-\mu_{\mathrm{As}}^B) - \frac{1}{2}\left(n_{\mathrm{Ga}} - \frac{n_{\mathrm{As}}}{2}\right)(\mu_{\mathrm{Ga}}^B - \mu_{\mathrm{As}}^B) - \frac{1}{4}(n_{\mathrm{In}}+n_{\mathrm{Ga}}+n_{\mathrm{As}})\mu_{\mathrm{InGaAs}_2} - \frac{1}{4}(n_{\mathrm{In}}-n_{\mathrm{Ga}})(\mu_{\mathrm{In}}^B - \mu_{\mathrm{Ga}}^B) - n_{\mathrm{C}}\mu_{\mathrm{C}}^B, \quad \text{(A5)}$$

which is independent of the chemical potentials of constituents. The formation energy Ω_D only depends on $\Delta\bar{\mu}$, $\delta\bar{\mu}$, μ_e, and μ_{C}. Note that $\Delta\bar{\mu}$ has the minimum (maximum) value in the As-rich (poor) limit, i.e., $-\Delta\bar{H}\leq\Delta\bar{\mu}\leq\Delta\bar{H}$, where $\Delta\bar{H}(=\mu_{\mathrm{In}}^B+\mu_{\mathrm{Ga}}^B+2\mu_{\mathrm{As}}^B-\mu_{\mathrm{InGaAs}_2})$ is calculated to be 1.80 eV. The parameter $\delta\bar{\mu}$ determines the Ga:In flux ratio and is restricted by the constraint, $-\frac{1}{2}(\Delta\bar{H}-\Delta\bar{\mu})\leq\delta\bar{\mu}\leq\frac{1}{2}(\Delta\bar{H}-\Delta\bar{\mu})$. Under As-rich conditions ($\Delta\bar{\mu}=-\Delta\bar{H}$), $\delta\bar{\mu}$ varies from $-\Delta\bar{H}$ (Ga-rich limit) to $\Delta\bar{H}$ (In-rich limit), while for cation-rich conditions ($\Delta\bar{\mu}=\Delta\bar{H}$) $\delta\bar{\mu}$ is equal to zero. In stoichiometric $In_{0.5}Ga_{0.5}As$, $\Delta\bar{\mu}=0$ and $\delta\bar{\mu}=0$.

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