Fluorine atoms in AlAs, GaAs, and InAs: Stable state, diffusion, and carrier passivation

Akihito Taguchi
NTT Basic Research Laboratories, 3-1 Morinosato Wakamiya, Atsugi-shi, Kanagawa 243-0198, Japan

Takahisa Ohno and Taizo Sasaki
National Research Institute of Metals, 1-2-1 Sengen, Tsukuba-shi, Ibaraki 305, Japan
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We investigated various basic properties of fluorine (F) atoms in AlAs, GaAs, and InAs by using first-principles calculations. In these three semiconductors, we found that the -1 charge state is the most stable in a wide range of Fermi levels and that the F atom prefers sites surrounded by group-III atoms. These characteristics can be understood by considering that F has the largest electronegativity among the elements. We found that the diffusion properties, such as the diffusion path and the diffusion barrier height, are similar in these semiconductors. The estimated barrier heights are also comparable to the experimentally obtained barrier height in $Al_{0.48}In_{0.52}As$, suggesting that the diffusion properties in $Al_xIn_{1-x}As$ are also similar. This implies that the experimentally observed selective F incorporation into $Al_xIn_{1-x}As$ is not due to the diffusion properties. It has been thought that the F atom forms a F-Si defect complex in $Al_xIn_{1-x}As$, but we found that a F atom in the -1 charge state has stability comparable to that of a F-Si defect complex in binary semiconductors, suggesting that F-Si defect complexes and isolated F atoms in the -1 charge state coexist in $Al_xIn_{1-x}As$. This coexistence is consistent with the observation of the F-Si defect complex, as well as observed F doping effects such as donor passivation and the decrease in the electron mobility. Based on the present calculations for the binary semiconductors, some characteristic properties of F in $Al_xIn_{1-x}As$ can be understood.

I. INTRODUCTION

The characteristic properties of halogen atoms in bulk semiconductors and the near-surface region are of great importance for various processes in device fabrication. Recently, a very peculiar phenomenon related to fluorine (F) was found in the $Al_xIn_{1-x}As/Ga_xIn_{1-x}As$ system. That is, F causes the degradation of electronic properties during thermal processes.[1,2] Due to F incorporation, the free electron concentration decreases (donor passivation) and the electron mobility also decreases.[2,3] In contrast to the *n*-type host, carrier passivation has not been observed in *p*-type $Al_{0.48}In_{0.52}As$.[4] Because the $Al_xIn_{1-x}As/Ga_xIn_{1-x}As$ system is promising for high-electron-mobility transistors, the degradation of the electronic properties is a serious problem.

The most pronounced characteristic feature of the degradation is high selectivity. The degradation is observed in $Al_xIn_{1-x}As$, but not in AlAs, GaAs, and InAs or in the other ternary semiconductors between these binary semiconductors. It has been confirmed that F atoms are incorporated from the surface by experiments under different annealing conditions[4] and investigations of the effect of cap layers.[5] The importance of the surface becomes clear, but to understand the high selectivity it is necessary to investigate F diffusion in the bulk. Diffusion of F atoms in $Al_xIn_{1-x}As$ bulk was thought to be fast because of the rather large spatial space in the interstitial region of the lattice.[6] However, since the diffusion properties of F atoms in other binary semiconductors and ternary semiconductors have not been investigated, it is not clear whether the fast diffusion is a unique property of $Al_xIn_{1-x}As$. The relation between the high selective nature and the diffusion properties is also not yet clear.

The F atoms in *n*-type $Al_xIn_{1-x}As$ may capture electrons because F has the largest electronegativity among the elements. Because the amount of the decrease in the carrier concentration is in good agreement with the F concentration,[2,4] one F atom captures one electron. Although F atoms in the -1 charge state explain both the donor passivation and the decrease in the mobility, experimental results that contradict this explanation have been reported by Hayafuji *et al.*[7,6] They claimed, based on comprehensive annealing experiments and bias-temperature tests, that F-Si defect complexes are formed in $Al_{0.48}In_{0.52}As$.[7] The formation of F-Si complexes was also suggested from the spectrum change due to Si doping in their Fourier transform infrared spectroscopy measurements.[6] The F-Si defect complex explains donor passivation but cannot explain the decrease in the mobility, because the concentration of the ionized impurity decreases due to the formation of the defect complexes. Therefore, more detailed investigations of the stable atomic configurations of F atoms in the hosts are required.

Many experimental studies have been carried out for the $Al_xIn_{1-x}As/Ga_xIn_{1-x}As$ system because of its technological importance, but theoretical studies have not been carried out. Although theoretical investigations of ternary semiconductors are difficult, the characteristic properties of F atoms in ternary semiconductors could be deduced from those in binary semiconductors. To understand the characteristics of F in the $Al_xIn_{1-x}As/Ga_xIn_{1-x}As$ system, an understanding of the characteristics of F in AlAs, GaAs, and InAs is necessary. Therefore, we have investigated various basic properties of F in these three binary semiconductors by using first-principles pseudopotential calculations. The next section explains the calculation method. Section III presents the calculated total energies of F at various interstitial sites and compares them by taking into account the Fermi level effect.

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We considered charge states from +1 to −1 to investigate the carrier passivation. The diffusion paths and the diffusion barrier heights are also estimated and discussed. We further investigated the defect complexes of F-Si and F-F to examine the donor passivation and the decrease in the electron mobility. We will show that many features are similar in the three semiconductors. The experimental results for $Al_xIn_{1-x}As$ are discussed based on the presently investigated properties of AlAs, GaAs, and InAs. The results and remaining problems are summarized in Sec. IV.

II. CALCULATION METHOD

We used the first-principles pseudopotential method based on the local density functional formalism. For Ga, Al, In, As, and Si, soft pseudopotentials with the form proposed by Troullier and Martin were used.[8–10] For F, the ultrasoft pseudopotential developed by Vanderbilt[11] was used.[12] The pseudo-wave-function was expanded by a plane-wave basis set. A 32-atom supercell was used and the lattice around the impurity atom(s) was optimized. We took four k points to carry out the k-space integration. The kinetic-energy cutoff was taken to be 20.25 Ry. The convergence of the differences in the total-energy between the different states was checked by calculations using a larger kinetic-energy cutoff of 36 Ry. The ambiguity in the total-energy difference among different states was estimated to be less than 0.2 eV by comparing the total energies of F^0 and F^- at interstitial sites in GaAs. The conjugate-gradient technique was used to optimize both the electronic structure and the atomic configuration.[13]

To determine the stable site of a F atom in AlAs, GaAs, and InAs, the total energies at the various interstitial sites shown in Fig. 1 were calculated. In the figure, T denotes the tetrahedral interstitial site and the C site is the center of the rhombus composed of three adjacent lattice atoms and the nearest T site. AB denotes the antibonding site. There are two kinds of T, C, and AB sites, depending on the kinds of atoms at the nearest neighbor site. Hence, the nearest neighbor atom is indicated as a subscript. The III represents Al, Ga, or In, depending on whether the lattice is AlAs, GaAs, or InAs. H denotes the hexagonal interstitial site and BC denotes the bond center site. M denotes the middle site between the neighboring $C_{\rm As}$ and $C_{\rm III}$ sites, but these two sites are not on the same (110) plane. Considering the $C_{\rm As}$ site in the figure, the nearest $C_{\rm III}$ site is not on the (110) plane shown, but it is above (or below) it. Hence, the M site is not on the (110) plane shown, either. In the figure, its projected position is shown.

We considered charge states from +1 to −1 to investigate the carrier passivation effect. The Fermi level effect was taken into account by calculating the formation energy.[14] To obtain the stable atomic configurations around a F atom, the F atom position was fixed at each site except for the BC site, and then the positions of the surrounding atoms were optimized. For the BC site, the F atom position was optimized on the (110) plane, since it was found that the ideal BC site is unstable and gives much higher energy than the relaxed BC site.

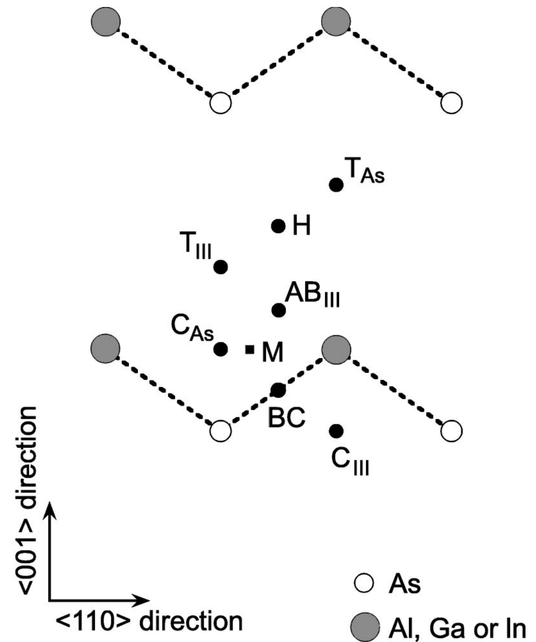

FIG. 1. Considered interstitial sites for F atoms. The (110) plane is shown. $T_{\rm III}$ denotes the tetrahedral interstitial sites surrounded by group-III atoms. The H site is the hexagonal interstitial site. BC denotes the bond-center site and AB denotes the antibonding site. The C site is the center of the rhombus formed by three adjacent lattice atoms and one T site. Since there are two kinds of C sites, depending on the nearest neighbor lattice atom, the atom is indicated. M is the middle site between the neighboring $C_{\rm III}$ and $C_{\rm As}$ sites. Because the M site is not on the (110) plane, its projected position on the (110) plane is shown.

III. RESULTS AND DISCUSSION

A. Stable state

We investigate the stable site by comparing the formation energies at various sites and considering their dependence on the Fermi level position. In determining the formation energy, the separated state of the III-V semiconductor bulk and an isolated F atom was taken as the reference state. Figure 2 shows the formation energy as a function of the Fermi level for (a) AlAs, (b) GaAs, and (c) InAs. The Fermi level was set to zero at the top of the valence band. The band gap was normalized by the calculated band gap of each bulk.

In Fig. 2(a), for the neutral and +1 charge states only the results for the most stable sites are shown, since it was found that the −1 charge state is the most stable in a wide Fermi level range. In the −1 charge state, the M, $T_{\rm Al}$, $C_{\rm As}$, and $AB_{\rm Al}$ sites have nearly the same energy and are the most stable. The reason why these sites have low energies can be understood by considering the electronegativity. The electronegativity of Al is smaller than that of As, and the F electronegativity is the largest among the elements. Therefore, a F atom prefers the region near Al atoms. The fact that F has the largest electronegativity can also qualitatively explain why sites near the As atom, such as $T_{\rm As}$ and $AB_{\rm As}$, show rather high energies. In GaAs [Fig. 2(b)] and InAs [Fig. 2(c)], it was also found that the −1 charge state is the most stable in a wide Fermi level range. The stable sites in these two semiconductors and those in AlAs show similar tendencies: the sites near group-III atoms show rather low

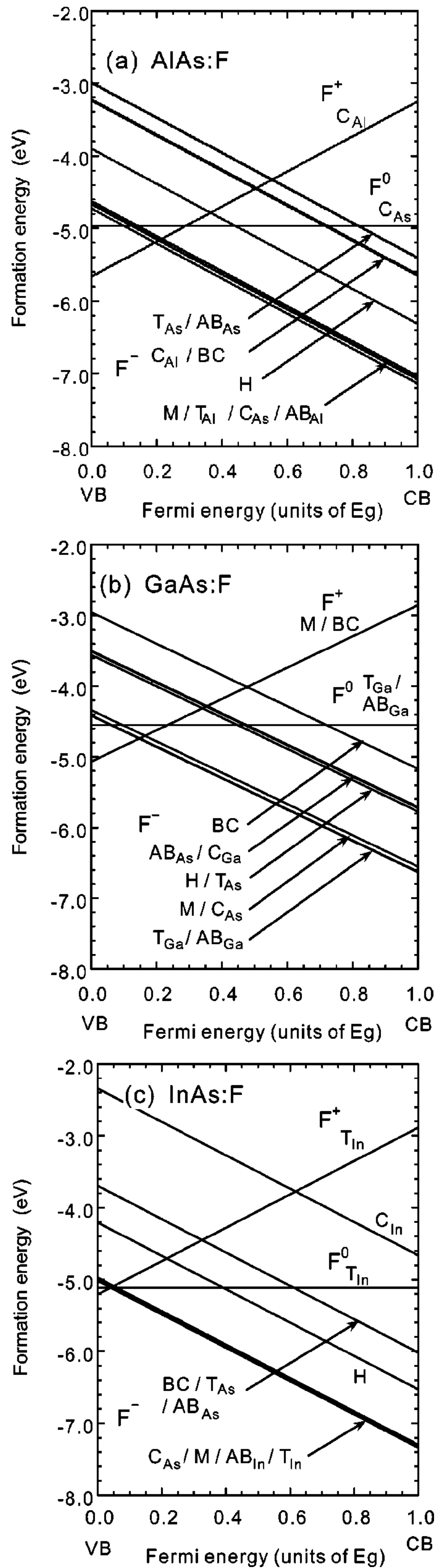

FIG. 2. Formation energies as a function of Fermi level for (a) AlAs, (b) GaAs, and (c) InAs. The formation energy was measured by taking the energy for the isolated F atom and the bulk as the reference. The Fermi level was measured by calculating the band gap of each bulk and the top of the valence band was taken as the reference in each material. Because it was found that the -1 charge state is the most stable, for the $+1$ and 0 charge states only the energy of the most stable site is shown.

energies, while the sites near As atoms show rather high energies. In every host, several sites, such as M, T_{III}, C_{As}, and AB_{III}, show nearly the same energy and are the most stable. This indicates that F atoms do not form strong bonds with the lattice atoms even in the most stable states. For F in Si, a similar stable property, i.e., that a F atom in the -1 charge state at the T site is the most stable, has been reported from the first-principles calculation results.[15]

Because in the three binary semiconductors the -1 charge state is the most stable in a wide Fermi level range, the -1 charge state is expected to also be the most stable in $\mathrm{Al}_x\mathrm{In}_{1-x}\mathrm{As}$. This implies that a F atom captures an electron in n-type $\mathrm{Al}_x\mathrm{In}_{1-x}\mathrm{As}$, resulting in donor passivation. The present calculation results show that F always results in the donor passivation regardless of the host. It seems that the experimentally observed selectivity of $\mathrm{Al}_x\mathrm{In}_{1-x}\mathrm{As}$ is due to the incorporation and/or diffusion properties of F and not due to its electronic properties of F.

At the top of the valence bands, the energy profits of the $+1$ charge states to the neutral charge states are 0.70 eV for AlAs, 0.55 eV for GaAs, and 0.09 eV for InAs. These energy profits are rather small and suggest that the $+1$ charge state is not so stable in the p-type ternary semiconductors composed of these binary semiconductors, although the local strain and its effect on the charge state in the ternary semiconductors are not yet clear. The unstableness of the $+1$ charge state could explain the experimentally observed absence of carrier passivation in p-type $\mathrm{Al}_{0.48}\mathrm{In}_{0.52}\mathrm{As}$.[4]

Although F shows features similar to AlAs, GaAs, and InAs, some differences can be seen when we investigate the atomic configurations in more detail. When we consider a F atom at the T_{III} site, which is the most stable site in every host, the distances between the F atom and the neighboring group-III atoms are 2.29, 2.34, and 2.45 Å in AlAs, GaAs, and InAs, respectively. These distances are shorter by 6.5%, 4.5%, and 6.6% in AlAs, GaAs, and InAs from the ideal distances. This suggests a weaker interaction of F with Ga than with Al or In.

B. Diffusion

In the preceding section, we showed that in every host F atoms are the most stable in the -1 charge state in a wide Fermi level range. The stable sites are in the low-valence-electron-density region. Therefore, F atoms are expected to diffuse in this region in n-type hosts. The diffusion paths may basically be the same in each host and may be $-T_{\mathrm{III}}-H-T_{\mathrm{As}}-H-$. To estimate the diffusion paths and diffusion barrier heights, we moved a F atom within the (110) plane. The F atom was slightly moved from the H site toward the T_{III} and T_{As} sites. Its position in the $\langle 110 \rangle$ direction was fixed, but the position along the $\langle 001 \rangle$ direction was optimized. The positions of the other atoms were fully optimized. Figure 3(a) shows the estimated diffusion paths. The F atom diffuses in the region where the valence-electron density is low, as expected.

The energies obtained along the estimated diffusion paths are shown in Fig. 3(b). The diffusion barrier height was estimated as the energy difference between the maximum and the minimum energies during the diffusion. The estimated barrier heights are 1.5, 1.0, and 1.3 eV for AlAs, GaAs, and

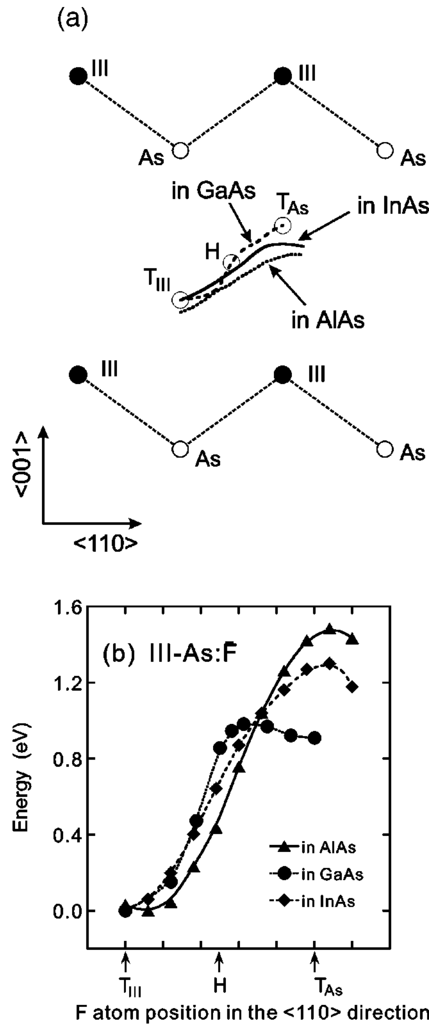

FIG. 3. (a) Estimated diffusion paths for AlAs, GaAs, and InAs on the (110) plane. (b) Energy profile during the diffusion. The arrows show the position in the ⟨110⟩ direction of the site indicated.

InAs, respectively. For AlAs and InAs, the energy potential profile shows a maximum near the T_{As} site, while the potential profile for GaAs has a maximum near the H site. When the energies at the T_{As} and H sites are compared [Figs. 2(a)–2(c)], they are almost the same in GaAs, but the energy at the T_{As} site is higher than that at the H site in AlAs and InAs. These relative energies are reflected in the energy profile, but the obtained energy profile seems strange. Because Al, Ga, and In are, respectively, in the third, fourth, and fifth rows of the periodic table, GaAs is expected to show intermediate properties between AlAs and InAs. Several physical properties actually show this expected tendency. Two examples are the order of the ion radius, which is Al$>$Ga $>$In, and the order of the III-As bond strength, which is AlAs$>$GaAs $>$InAs.[16] The reason why the energy profile in GaAs is different from those in AlAs and InAs is not clear yet. The difference in F's reactivity with the group-III elements and local lattice strain would be related to the difference in the energy potential profiles.

The estimated diffusion barrier heights in the three semiconductors do not show much difference, indicating that the diffusion properties of F atoms in these binary semiconductors are similar. Therefore, in $Al_xIn_{1-x}As$ the diffusion properties are expected to also be similar. This expectation is supported by the fact that the experimentally obtained diffusion barrier height in $Al_{0.48}In_{0.52}As$, 1.13 eV, is close to those presently estimated in the binary semiconductors.[7] These findings strongly suggest that the selective degradation in $Al_xIn_{1-x}As$ due to F is not determined by the diffusion properties of F.

The dependence of the thermal diffusion of F atoms on conductivity has been systematically investigated by using superlattice structures comprising several n-type AlInAs layers with semi-insulating (SI) AlInAs layers between them.[5] The F concentration was measured by secondary ion mass spectroscopy (SIMS) after the annealing. It was found that the F concentration is very low in the SI layers, but that F atoms diffuse into the deeper n-type layers across the SI layers. This indicates that F atoms diffuse in the SI layers rather easily. The low concentration of F in SI layers is due to the unstable nature of F in those layers. This is consistent with the present calculation results showing that the -1 charge state is much more stable than the neutral charge state.

When F diffuses from an n-type layer to a SI layer, the Fermi level changes from its position near the bottom of the conduction band to a position near the middle of the band gap. In all three semiconductors, the -1 charge state is still the most stable charge state at the middle of the band gap [Figs. 2(a)–2(c)]. Therefore, a F atom may diffuse from the n-type layer to the SI layer keeping the -1 charge state. The energy corresponding to the change in the Fermi level acts as a diffusion barrier. In such a case, an additional electrostatic potential is produced by the Coulomb interaction between the F^- atoms in the SI layer and the positively charged donor atoms in the n-type layer. The electrostatic potential disturbs the diffusion. Therefore, the sum of the Fermi level change and the additional electrostatic potential acts as the effective diffusion barrier. Because the estimation of the additional electronic potential is difficult, the effective diffusion barrier height cannot be exactly estimated. However, the effective barrier height must be equal to or smaller than the energy necessary to change the charge state from -1 to 0. If the Coulomb interaction is strong, the F^- atom will release the captured electron and become neutral. In such a case, the energy necessary to change the charge state corresponds to the effective diffusion barrier. The required energy in the charge state change can be estimated as the energy difference between F^- and F^0 at the bottom of the conduction band, and it is nearly the same in the three semiconductors, ~ 2 eV. The diffusion barrier between the n-type layers and SI layers in addition to the unstable nature of F in SI layers may be the reason why a very low F concentration[5] and a rapid decrease in the F concentration[2] have been experimentally observed.

C. Coupled structure and carrier passivation

Because F-Si defect complexes have been suggested,[6,7] we investigated the formation of such complexes. We examined the coupling of a F atom with a Si atom, assuming that a Si atom substitutes for the group-III atom. In the calculations for the F-Si defect complexes, one F atom was put near the Si atom, then the atom positions, including those of the

Si and F atoms, were optimized. The F atom position was optimized within the (110) plane. We consider the formation process to be as follows

$$F+Si_{III}\leftrightarrow F\text{-}Si.$$

In the left-hand side of the reaction, the F and Si atoms were assumed to be spatially separated. It was assumed that a F atom is in the neutral charge state and occupies the most stable *T* site. We compared the total energy between the left-hand and right-hand sides of the reaction, and found that the total energy decreases in every host with the formation of F-Si complexes. Here, we define the binding energy of the complex as the total-energy difference between the left-hand and right-hand sides of the above reaction. The estimated binding energies are 2.2, 2.5, and 1.8 eV in AlAs, GaAs, and InAs, respectively. Because the binding energy in GaAs is the largest, the binding of F with Si must be strongest in GaAs. Such strong binding appears as the shortest distance between the F and Si atoms in GaAs. The distance is 1.73 Å in GaAs, while the distances are 2.78 and 2.80 Å in AlAs and InAs, respectively.

The present calculation results show that F and Si atoms form stable defect complexes in the binary semiconductor hosts, suggesting that F-Si complexes are stably formed in the ternary semiconductors. As mentioned, the F-Si complex in $Al_{0.48}In_{0.52}As$ has actually been suggested based on the experiments.[6,7] If the F-Si defect complex is very stable and all F atoms couple with Si atoms, the electron mobility does not decrease due to the F incorporation, because F-Si complexes are neutral and thus less effective carrier-scattering centers. Because the F-Si complexes contradict the experimental results, we compared the stability of the F-Si complex with that of an isolated F atom. Considering the defect complex formation process, the formation energy of F-Si can be estimated as the energy that is smaller than that of F^0 by the binding energy. The estimated formation energies along with the energies of the charge states are shown in Figs. 4(a) for AlAs, 4(b) for GaAs, and 4(c) for InAs. In the figures, the formation energies of F-F defect complexes, which were determined in the same manner, are also shown, and will be discussed later. In AlAs [Fig. 4(a)], the energies of the F-Si defect complex and the F^- are nearly equal at the bottom of the conduction band. In GaAs, the energy of the defect complex is lower than that of the F^- by 0.41 eV, while in InAs it is higher by 0.44 eV. These energy differences are rather small considering the annealing temperature. Hence, it is expected that some of the F atoms do not form defect complexes and remain in the -1 charge state, so that both F-Si defect complexes and isolated F atoms in the -1 charge state exist in the host at the same time. Both the isolated F^- atoms and the ionized Si donor atoms reduce the mobility, because they are efficient ionized scattering centers. The isolated F atoms capture electrons to take the -1 charge state, resulting in the decrease in the free-electron concentration. The F-Si complexes also make the free-electron concentration low, because they cannot be donors. Therefore, the amount of the decrease in the electron concentration equals the F concentration. This has actually been observed in experiments.[2,4] Therefore, the coexistence of F^- and F-Si complexes explains all the reported characteristic properties due to the F doping: donor passivation, the decrease in the electron mobility, and the observation of F-Si complexes.

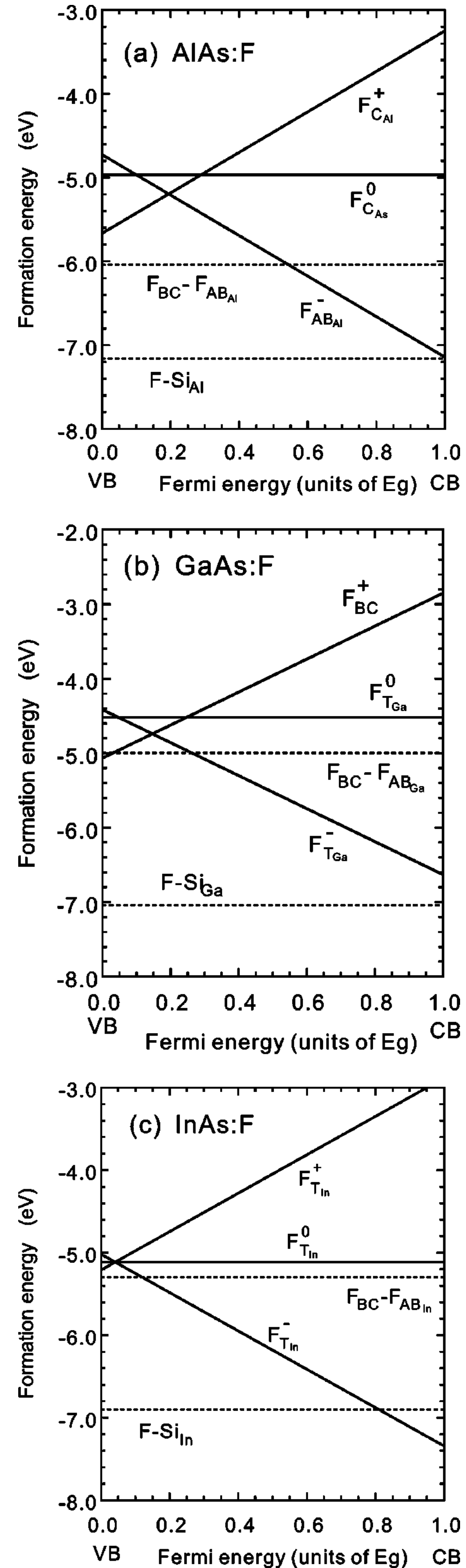

FIG. 4. Formation energies of the F-Si complex and F-F complex as a function of the Fermi level for (a) AlAs, (b) GaAs, and (c) InAs. The most stable states for -1, 0, and $+1$ charge states are shown for comparison.

Light elements sometimes form a stable molecular structure in bulk materials. The hydrogen molecule in Si, for in-

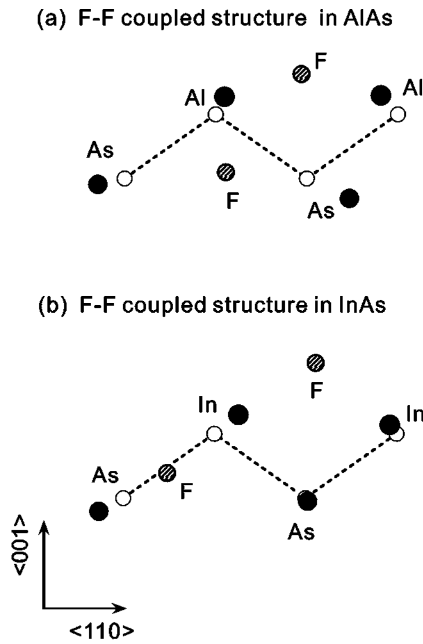

FIG. 5. Optimized atomic configurations of the F-F defect complexes in (a) AlAs and (b) InAs. Open circles indicate the ideal lattice sites. Hatched circles denote F atoms, and the closed circles denote Al, In, and As atoms.

stance, is well known.[14] We considered the F-F defect complex to investigate the formation of the F_2 moleculelike structure. We put two F atoms on the same (110) plane, and their positions were optimized within the plane. The lattice around the F-F pair was fully optimized.

When the two F atoms were put near the T_{III} site, the distance between them increased during the optimization process, and the F-F defect complex was found to be unstable in all three semiconductors considered here. However, when we put one F atom at the AB_{III} site and the other at the BC site, the F-F defect complex became stable in every host. The estimated formation energies for such stable F-F defect complexes are shown in Figs. 4(a) for AlAs, 4(b) for GaAs, and 4(c) for InAs.

In the three hosts, the F-F defect complex is more stable than the two separated F^0 atoms, but at the bottom of the conduction band the -1 charge state is much more stable than the F-F defect complex. Therefore, in *n*-type hosts, the F-F defect complex is not formed, which means that the F^- and the F-Si defect complex are the origin of the donor passivation. At the top of the valence band, the F-F defect complex is more stable than the $+1$ charge state in AlAs, and is comparably stable in GaAs and InAs. Therefore, the F-F defect complexes might be formed in *p*-type hosts. The F-F defect complex could be one possible explanation for the absence of carrier passivation in *p*-type materials.

The formation energies of F-F defect complexes are smaller than those of the F^0 atoms by 1.07 eV in AlAs, 0.48 eV in GaAs, and 0.18 eV in InAs. The largest energy profit in AlAs suggests strong interactions of F atoms with lattice atoms in AlAs. The optimized atomic configurations of the F-F structures are shown in Fig. 5 for AlAs and InAs. In AlAs, one F atom was put at the BC site before the optimization, but it moved and situated near the C_{Al} site after the optimization. In contrast, a F atom remains at the BC site in InAs, and the As–F–In–F atoms are almost aligned. In GaAs, the atomic configuration is quite similar to that in InAs. Although the reason for the difference in the F-F atomic configurations is not clear, it may be related to the binding nature of F to the group-III atoms. The large modification of the atomic configuration in AlAs is consistent with the speculated strong interaction between the F atoms and lattice atoms.

IV. SUMMARY

We investigated various basic properties of F in AlAs, GaAs, and InAs by using first-principles calculations. We found that the -1 charge state is the most stable in a wide range of Fermi levels in these semiconductors. We also found that the stability of the sites is similar in these semiconductors: the sites near the group-III atom are rather stable, while the sites near the As atoms have rather high energies. The estimated diffusion paths in the -1 charge state are also similar in each host. F atoms diffuse in the low-valence-electron-density regions. The fact that F has the largest electronegativity among the elements may be the main factor determining these properties. The estimated diffusion barrier heights are close among the three semiconductors and also close to that experimentally obtained for $Al_{0.48}In_{0.52}As$. Therefore, the diffusion properties depend little on the host. This suggests that the experimentally observed selective nature of F in $Al_xIn_{1-x}As$ is not due to diffusion.

Although the F properties in the ternary semiconductor of $Al_xIn_{1-x}As$ have not yet been theoretically investigated, some of the experimental results can be explained based on the present results for binary semiconductors. The most stable property of the -1 charge state in the binary semiconductors strongly suggests that the -1 charge state is also the most stable in $Al_xIn_{1-x}As$. The unstable property of the neutral charge state is consistent with the experimentally observed low F concentration in SI layers. Although it was suggested that F atoms form F-Si defect complexes in $Al_xIn_{1-x}As$, the F-Si complex cannot explain the decrease in mobility. The present calculation results for the binary semiconductors suggest that the F-Si defect complex and the isolated F^- atom have a similar stability and thus may coexist in $Al_xIn_{1-x}As$. If this is the case, the coexistence explains the decrease in the mobility, as well as the donor passivation and the observation of the F-Si pair.

Although the electronic property degradation in $Al_xIn_{1-x}As$ can be explained based on the present investigations for binary semiconductors, the selective nature of the degradation is still unclear. This is because the present calculations show that the properties of F are very similar in the three binary semiconductors, suggesting the degradation has little dependence on the host. To reveal the selective nature of the degradation, the surface effect, which determines the incorporation of F atoms into the hosts, has to be investigated in detail.

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