Mutual Passivation of Donors and Isovalent Nitrogen in GaAs

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We study the mutual passivation of shallow donor and isovalent N in GaAs. We find that all the donor impurities, Si_{Ga}, Ge_{Ga}, S_{As}, and Se_{As}, bind to N in GaAs:N, which has a large N-induced band-gap reduction relative to GaAs. For a group-IV impurity such as Si, the formation of the nearest-neighbor Si_{Ga}-N_{As} defect complex creates a deep donor level below the conduction band minimum (CBM). The coupling between this defect level with the CBM pushes the CBM upwards, thus restoring the GaAs band gap; the lowering of the defect level relative to the isolated Si_{Ga} shallow donor level is responsible for the increased electrical resistivity. Therefore, Si and N mutually passivate each other's electrical and optical activities in GaAs. For a group-VI shallow donor such as S, the binding between S_{As} and N_{As} does not form a direct bond; therefore, no mutual passivation exists in the GaAs:(S + N) system.

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Band-gap engineering in semiconductors is usually carried out through alloying, where the band gap of the alloy $A_{1-x}B_xC$ changes continuously from the band gap of AC to the band gap of BC as a function of alloy concentration x [1,2]. In some cases, the band gap can be further tuned by controlling the ordering parameter of the semiconductor alloys [3,4]. Recently, it has been shown that mutual passivation of defect pairs in semiconductors could also be used to tune the band gap and control materials' transport properties [5–10]. One of the well-studied examples is the mutual passivation of H and N in GaAs. Nitrogen profoundly affects the electronic structure of GaAs. Adding a few percent of N can drastically lower the band gap of GaAs [11–14]. However, when H is incorporated into the N-doped sample, a complete reversal of the drastic band-gap reduction caused by N is observed [5]. On the other hand, hydrogen, which is an amphoteric defect in GaAs compensating both donors and acceptors [15], does not have this property when N is introduced, suggesting a strong mutual passivation between hydrogen and nitrogen in diluted III-V nitride alloys. To explain this unusual behavior, Janotti *et al.* [6] have proposed that this mutual passivation is caused by the strong bonding between nitrogen and hydrogen and the formation of $H_2^*(N)$ defect complexes. In this case, the bonding of the first H, H(1), to N leads to large atomic displacements along the $\langle 111\rangle$ direction, breaking one of the Ga-N bonds and creating a Ga dangling bond (DB)-like state near the conduction band minimum (CBM). The bonding of the second H, H(2), to the Ga atom then eliminates this DB-like state and creates a bonding state below the valence band maximum (VBM) and an antibonding state inside the conduction band of GaAs; therefore, it opens up the band gap by removing the band-gap reduction caused by N incorporation at the As site.

Recently, new experiments by Yu *et al.* [7–10] have demonstrated that Si substitution on the Ga site and N on the As site can also passivate each other's electrical and optical activities. They find that adding Si to N-doped GaAs (GaAs:N) can remove the effect of N, increasing its optical band gap. On the other hand, adding N to Si-doped GaAs (GaAs:Si) decreases the electron carrier density provided by the Si donor and sharply increases its electric resistivity. They attribute these behaviors to mutual passivation of Si and N in GaAs by forming Si-N defect pairs. Similar effects are also observed in Ge- and Sn-doped InGaAsN thin films [8–10]. However, surprisingly, this mutual passivation effect does not exist in S- or Se-doped InGaAsN samples [7,8,16,17]. Yu *et al.* speculated that this could be an indication that S or Se does not bind with N in GaAs [7,8].

One may be inclined to compare the Si_{Ga}-N mutual passivation with the H-N mutual passivation by mutating Si into H + Ga. However, there are some fundamental differences between these two system: (i) H + Ga is much more electronegative than Si. H + Ga creates a singly occupied level near the VBM, so it is characterized as an acceptor; but Si_{Ga} creates a shallow donor level below the CBM. (ii) $H_2^*(N)$ is a neutral defect, whereas the Si_{Ga}-N_{As} defect pair should still be a donor. Therefore, the formation of $H_2^*(N)$ is able to completely remove defect levels from the band gap; but for Si_{Ga}-N_{As}, some defect levels are expected to exist inside the gap. (iii) The binding of $H_2^*(N)$ is mostly due to the charge transfer from H + N_{As} to H + Ga and the resulting Coulomb interaction. The binding for Si_{Ga}-N_{As} is expected to be due mostly to the Coulomb attraction of the more positively charged Si_{Ga} to the more negatively charged N_{As}. Based on this understanding, however, it is difficult to explain why N_{As} does not bind with S_{As} and Se_{As}, because, like Si_{Ga}, they are also shallow donors in GaAs, although the S_{As}-N_{As} distance is slightly longer than that of the nearest-neighbor Si_{Ga}-N_{As} bond. These analyses suggest that the mutual passivation between Si and N in GaAs should have a very different origin from that of H and N in GaAs.

To understand these puzzling but interesting experimental observations on the mutual passivation of defects, we have performed first-principles total-energy and band-structure calculations. We find that all the donor impurities, Si_{Ga}, Ge_{Ga}, S_{As}, Se_{As}, bind to N in GaAs:N. For a group-IV impurity such as Si, the formation of the nearest-neighbor Si_{Ga}-N_{As} defect complex creates a deep donor level below the CBM. The coupling between this defect level with the CBM pushes the CBM upwards, thus increasing the band gap, whereas the lowering of the defect level relative to the shallow level of isolated Si_{Ga} is responsible for the increased electrical resistivity. However, unlike the H-N passivation [forming $H_2^*(N)$], where all the gap levels are removed, Si-N mutual passivation now converts Si_{Ga} from a shallow donor to a deep one. For a group-VI impurity such as S, the Coulomb binding between S_{As} and N_{As} does not form a direct bond and a deep level inside the gap; so the N isovalent level is still above the CBM, pushing the CBM downwards, whereas S_{As} still behaves as a shallow donor in GaAsN. That is, there is no mutual passivation in the GaAs:(S + N) system.

Method of calculations.—Our calculations are performed within the local density approximation (LDA) [18] as implemented in the pseudopotential VASP code [19]. The binding energy and atomic displacement around the defects are calculated using LDA for supercells up to 512 atoms per cell. For large supercells up to 4096 atoms per cell, we have adopted the charge patching method (CPM) [20,21]. In the CPM, a medium-size cell (64 or 512 atoms) with a defect is fully relaxed using LDA quantum mechanical forces, except for the atoms at the cell boundaries, which are fixed at their ideal positions. For larger supercells, the charge density of the calculated medium-size cell is patched to the outer region using the charge densities of pure bulk compounds. The generated charge density $\rho(\mathbf{r})$ of the large supercell is then used to obtain the potential $V(\mathbf{r})$. After that, the standard Kohn-Sham equations are solved using the folded spectrum method [22] for a few states near the band gap.

A 65 Ry kinetic energy cutoff for the plane-wave basis set is used. The present plane-wave pseudopotential LDA calculations give band gaps of 0.68 and 1.75 eV for bulk GaAs and GaN, respectively, smaller than the experimental value of 1.52 and 3.29 eV [23]. To correct the LDA band-gap error, we modified the nonlocal potential of the Ga, As, and N pseudopotentials [20,24] where the parameters are fitted to the experimental energy levels of the binary compounds GaN and GaAs. This procedure is used only for the final-stage band-structure calculations, whereas the total energy and structural relaxation are performed within the LDA. The transferability of the fitted pseudopotential has been tested extensively [20,21]. Furthermore, because we study here the variation of the defect levels before and after the formation of defect complexes, we expect that the residual error due to the fitting is largely cancelled.

Stability of the defect pairs.—The stability of the defect pair at low temperature is determined by its binding energy, defined as

$$E_b = E_{\text{tot}}(\text{GaAs:N} + X) + E_{\text{tot}}(\text{GaAs}) - E_{\text{tot}}(\text{GaAs:N}) - E_{\text{tot}}(\text{GaAs:}X), \quad (1)$$

where X is the defect-forming pair with N, and E_{tot} is the total energy, calculated using the same supercell at the neutral charge state. Negative E_b indicates that the defect binds to N. The calculated binding energies of the defect pair (N-X) are given in Table I. We find that the calculated E_b values are all negative; that is, all the donor defects form defect pairs with N, even at the neutral charge state. The magnitude of the binding energies decreases from Te to Se to S and O. This is consistent with the fact that the binding is mainly due to Coulomb binding between the donor defect and N, which is much more electronegative than the host As atom. As the donor electronegativity increases from Te to O, the Coulomb binding energy decreases. The large binding energy for large anions also reflects the strain compensation between the small N atom and the large anions. The reason that Ge has a smaller binding energy than Si can also be attributed to the fact that Ge is more electronegative than Si. Our calculations for Si and Ge are consistent with Yu *et al.*'s observations [7–10]. However, in contrast to their speculation, we find group-VI donor substitution on the As site to be attractive to N also.

Energy level of the point defects.—We calculated the energy levels of GaAs:Si, GaAs:S, and GaAs:N as a function of the size of the supercell containing 64, 512, 1728, and 4096 atoms per cell (corresponding to an impurity concentration of $x = 3.125\%$, 0.391%, 0.116%, and 0.049%, respectively). The energy levels are analyzed by projecting the wave function ψ_i in terms of Bloch states $\{\phi_{n,k}\}$ of the zinc-blende (ZB) bulk compounds. The energy levels of the three lowest conduction band states at $\bar{\Gamma}$ (Brillouin zone center of the supercell) as functions of the size of the supercell are shown in Fig. 1. The spectral projection $\sum_n |A_{n,k}|^2$ for $k = \Gamma$, X, and L of the states in the largest 4096-atom cell are also shown in the figure. From these analyses, we are able to identify the origin of these states.

We find that, in the impurity limit, Si creates a shallow donor level at about 10 meV below the CBM, in good

TABLE I. Calculated binding energies of defect pair N-X.

	Si	Ge	O	S	Se	Te
E_b (eV)	−0.26	−0.12	−0.06	−0.23	−0.29	−0.41

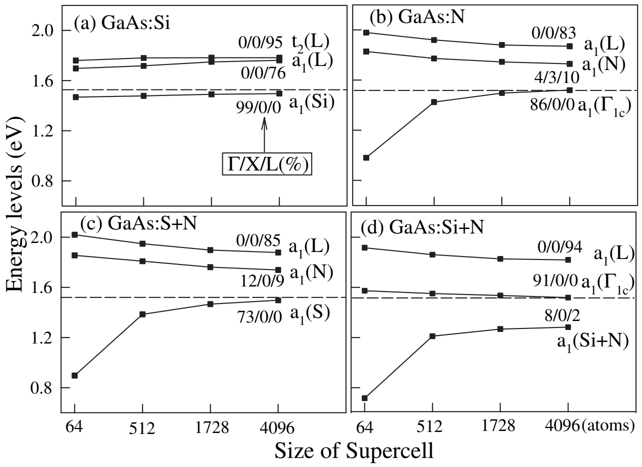

FIG. 1. Energy levels of the three lowest conduction band states in (a) GaAs:Si, (b) GaAs:N, (c) GaAs:S + N, and (d) GaAs:Si + N, as functions of the size of supercell. The percentages of $\Gamma/X/L$ characters for the states of the 4096-atom cell are also shown. The solid line connecting the dots is to guide the eyes only. The dashed line is the position of bulk GaAs CBM.

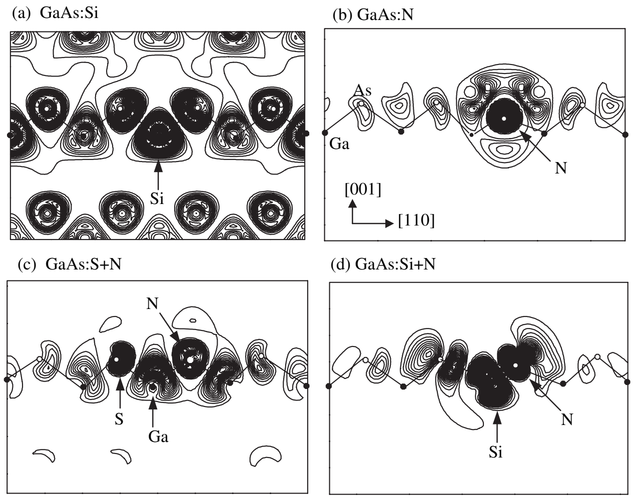

FIG. 2. The electron charge distribution of (a) a a_1(Si) state in GaAs:Si, (b) a a_1(N) state in GaAs:N, (c) a a_1(N) state in GaAs:S + N, and (d) a a_1(Si + N) state in GaAs:Si + N.

agreement with experiment [23]. Its position is not sensitive to the cell size or concentration. The wave function of the defect level is nearly pure Γ-like. The plotted charge distribution of the a_1(Si) in Fig. 2(a) shows that it is largely delocalized and has the ZB Γ_{1c} antibonding character, which is consistent with the fact that they are very shallow. The situation for GaAs:S (not shown) is very similar to that of GaAs:Si. For GaAs:N, due to the large size and chemical mismatch, an isovalent defect level a_1(N) at about 210 meV above the CBM appears in the impurity limit, in good agreement with the experimental measurement of 180 meV [25,26]. The plotted charge distribution of the a_1(N) impurity state in Fig. 2(b) shows that the impurity is strongly localized on the N site. This level, together with other a_1 levels in the conduction band, couples strongly with the CBM $a_1(\Gamma_{1c})$ state, lowering the energy of CBM and reducing the band gap [27]. We find that the energy level of the CBM is very sensitive to the cell size or N concentration, consistent with the fact that the alloy band-gap bowing parameter of $GaAs_{1-x}N_x$ is very large [13].

Energy level of the defect pairs and the mutual passivation effects.—The three lowest conduction band energy levels of GaAs:S + N at $\bar{\Gamma}$ as a function of the supercell size are shown in Fig. 1(c). We find that the variations of these levels are very similar to those in GaAs:N. The a_1(S) state is derived mostly from the CBM of GaAs:N. Its energy traces the CBM of GaAs:N and is at about 10 meV below the GaAs:N CBM; i.e., it still behaves as a shallow donor. The a_1(N) level is still resonant inside the conduction band. In the impurity limit, it is located at about 200 meV above the GaAs CBM. This indicates that there is no mutual passivation between S_{As} and N_{As}. In this system, S_{As} still behaves as a shallow donor in GaAs:N, and N still causes a large band-gap reduction in GaAs:S. To understand this, we plotted in Fig. 2(c) the charge distribution of the a_1(N) state in this system. It is clear from this plot that, in GaAs:S + N, S and N, sitting at the fcc anion sublattice sites [Figs. 2(c) and 3(a)], do not form a direct bond between them; thus, no new defect levels are created, and the shallow S-induced donor level and the N-induced resonant level do not passivate each other.

The situation for GaAs:Si + N is very different. The three lowest conduction band energy levels of GaAs:Si + N at $\bar{\Gamma}$ as a function of the supercell size are shown in Fig. 1(d). We find that the formation of the Si_{Ga}-N_{As} nearest-neighbor bond removed the a_1(N) level above the CBM. Instead, it creates a deep donor level at about 230 meV below the CBM in the impurity limit. This defect level has a weak CBM character and is strongly localized on the Si-N bond, as shown in Fig. 2(d) of the charge-density plot of the a_1(Si + N) state. The reason that this deep donor level can form could be understood by noticing that Si is more electronegative than Ga and N is more electronegative than As. The attraction of N towards Si [Fig. 3(b)] also increases the Ga-N bond from 2.04 Å in GaAs:N to 2.12 Å in GaAs:(Si + N). Therefore, the combined chemical effect and the bond relaxation near N pull this defect level down. To further verify that the lowest level in Fig. 1(d) is indeed a defect level, not a CBM derived state, we have calculated the optical transition matrix element M_{ij} from the VBM to the three lowest states at $\bar{\Gamma}$. We find that M_{ij} from the VBM to $a_1(\Gamma_{1c})$ state is about 0.2 a.u., similar to that in bulk GaAs, whereas M_{ij} from the VBM to the a_1(Si + N) state is one order smaller. This confirms our characterization of the energy levels in this system as shown in Fig. 1(d). The creation of these defect levels leads to the following consequences: (i) The shallow Si donor level in GaAs now becomes a deep Si + N donor

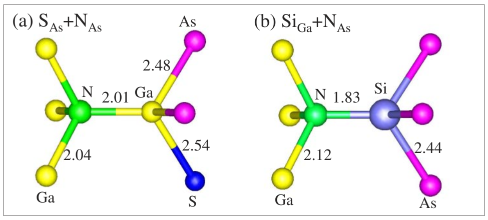

FIG. 3 (color online). Atomic structures of (a) S + N and (b) Si + N complexes in GaAs. The calculated ideal GaAs bond length is 2.42 Å.

level. This indicates that adding N to GaAs:Si can drastically reduce the electron carrier density, thus reducing the material's conductivity. (ii) The CBM $[a_1(\Gamma_{1c})]$ state, originally pushed down by the a_1(N) and other high-lying a_1 states in GaAs:N, is now also pushed upwards by the a_1(Si + N) state in GaAs:Si + N. The net effect is that the energy of the CBM is close to or slightly higher than the CBM in pure GaAs. This indicates that adding Si to GaAs:N can effectively remove the N-induced band-gap reduction in GaAs:N, therefore recovering the band gap. These results indicate that Si and N mutually passivate each other by forming the Si_{Ga}-N_{As} defect pair, reducing their effect on the optical and transport properties of GaAs. To further test this conclusion, we have done calculations for GaAs:(N, Si), where Si is in a position far from N. The calculated results are very similar to that found for GaAs:S + N, indicating that the mutual passivation does not exist if Si and N do not form a bond, as expected.

Comparison with experimental measurements.—Our results are consistent with the recent experimental observation [7–10] that Si (Ge) and N mutually passivate each other, whereas S (Se) and N do not show mutual passivation. Our analysis shows that the passivation mechanism for GaAs:Si + N is different from that in GaAs:H + N. One of the major differences is that, in GaAs:Si + N, the Si donor level is not removed from the band gap; it only changes from a shallow level to a deep level and, thus, could have a significant effect on the material's transport properties. Experimentally, the mutual passivation between Si and N is accompanied by the enhancement of deep-defect-level photoluminescence. Our calculations show that the a_1(Si + N) level is located at 0.23 eV below the GaAs CBM at the impurity limit. Experimental tests of our predictions are called for.

In summary, using the pesudopotential large-supercell calculations (up to 4096 atoms), we have studied the mutual passivation mechanism of isovalent N and donors in GaAs. We find that, unlike N_{As} in GaAs:N, which creates a resonant isovalent defect level inside the conduction band, the formation of the nearest-neighbor Si_{Ga}-N_{As} pairs creates a deep donor level in the gap. The coupling between this deep donor level and the conduction band restores the band gap of GaAs:N. On the other hand, the lowering of the defect level relative to shallow level of the isolated Si_{Ga} is responsible for the increased electrical resistivity in Si-doped GaAs:N. For a group-VI donor such as S, we find that, although they also bind to N, they do not form a direct bond with N; thus, there is no mutual passivation between S and N in GaAs. Our study, therefore, explained some of the recent puzzling experimental observations and provides a better understanding of band-gap engineering through mutual defect passivation.

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