Mutual Passivation of Electrically Active and Isovalent Impurities in Dilute Nitrides

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Using first-principles calculations we investigate the mutual passivation of shallow donor Si and isovalent N in dilute GaAsN alloys. Instead of the recently proposed pairing of Si and N on adjacent substitutional sites (SiGa–NAs) [K. M. Yu et al., Nat. Mater. 1, 185 (2002); J. Li et al., Phys. Rev. Lett. 96, 035505 (2006)] we find that N changes the behavior of Si in dilute nitride alloys in a more dramatic way. N and Si combine into a deep-acceptor split interstitial, where Si and N share an As site [(Si-N)As], with a significantly lower formation energy than that of the SiGa–NAs pair in n-type GaAs and dilute GaAsN alloys. The formation of (Si-N)As explains the GaAs band-gap recovery and the appearance of a photoluminescence peak at −0.8 eV. This model can also be extended to Ge-doped GaAsN alloys, and correctly predicts the absence of mutual passivation in the case of column-VI dopants.

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Alloys of highly mismatched semiconductors offer unique opportunities for band-structure engineering. For example, when a small fraction of As atoms in GaAs is replaced by N to form GaAsN alloys, the band gap changes rapidly with increasing N concentration, decreasing by as much as 180 meV per atomic percent of N [1–4]. This behavior is markedly different from that of conventional alloys [5]: one would expect the band gap of GaAs1–xN(x) to increase from its value in GaAs (1.5 eV) towards its value in GaN (3.4 eV) as the N content increases. This unusual behavior is of interest not only from a fundamental perspective, but also because of its significant potential in device applications [6].

As for any semiconductor, doping is essential for controlling the electrical conductivity in GaAs1–xN(x) alloys. While the physics of n-type and p-type doping in the parent compounds GaAs and GaN is well established, doping in GaAs1–xN(x) is much less explored. Recent reports indicate that the interaction between extrinsic dopants and N in GaAs1–xN(x) alloys can lead to entirely new phenomena [7–10]. Yu et al. [7] reported that when GaAs1–xN(x) is doped with Si, the interaction between Si and N leads to a “mutual passivation,” characterized by an increase in the band gap and an elimination of the electrical activity of the Si donor. It was observed that rapid thermal annealing of Si-doped dilute (In)GaAsN alloys at temperatures above 800 °C leads to a drastic increase in the electrical resistivity, accompanied by an increase in the band gap up to a value corresponding to the net “active” N, roughly equal to the total N concentration minus the Si concentration [7–9]. Simultaneously, a peak at −0.8 eV appeared in the photoluminescence spectra [7,8]. Similar effects were observed for Ge-doped, but not for S- or Se-doped GaAs1–xN(x) [9]. It was postulated that substitutional SiGa and GeGa form strong bonds with NAs and lead to deep donor levels, eliminating the shallow-donor character of Si and Ge in GaAs1–xN(x) alloys. On the other hand, SAs and SeAs are (at best) second-nearest neighbors of NAs and not directly bonded to NAs; therefore they would not suffer from the passivation effect [7–9].

First-principles calculations by Li et al. suggested that the SiGa–NAs complex [Fig. 1(a)] indeed induces a deep donor level in the band gap [11]; it was predicted that in the impurity limit this state would be located at 0.23 eV below the GaAs conduction-band minimum (CMB) [11]. Li et al. also reported a binding energy of 0.26 eV for the SiGa–NAs pair in the neutral charge state [11]. However, this proposed model exhibits some serious problems and discrepancies with experiment. First, a binding energy of 0.26 eV is too small to explain the formation of a high concentration of SiGa–NAs pairs at temperatures above 800 °C. At these temperatures, we estimate that less than 40% of the Si atoms would be bonded to NAs in SiGa–NAs pairs. Second, as will be shown later, their binding energy of 0.26 eV is overestimated. With a corrected binding energy, the number of complexes formed would be much smaller, in contrast to the experimental results [7–9]. Finally, the SiGa–NAs pair does not explain the appearance of a deep-level luminescence at −0.8 eV above the valence-band maximum (VBM) as observed in the experiments of Yu et al. [7,9].

In this Letter we show that isovalent N changes the microscopic behavior of Si donors in dilute GaAsN alloys.
in a more dramatic way. Based on first-principles density-functional calculations we find that Si combines with N into stable (Si-N)\textsubscript{As} split interstitials that act as compensating centers in \textit{n}-type GaAsN. The (Si-N)\textsubscript{As} split interstitial is a \textit{deep acceptor} with a formation energy that is significantly lower than that of Si\textsubscript{Ga}\textsubscript{As}\textsubscript{N} in \textit{n}-type GaAsN. The calculated acceptor level is located at 0.89 eV above the valence-band maximum. This explains the appearance of the photoluminescence peak that accompanies the mutual passivation effect. The formation of (Si-N)\textsubscript{As} split interstitials also leads to a blueshift in the band gap by reducing the nitrogen concentration that effectively participates in the band-gap reduction in GaAsN alloys. The formation of (Si-N)\textsubscript{As} split interstitials in annealed Si-doped GaAs\textsubscript{1-x}N\textsubscript{x} therefore leads to highly resistive alloys with a band gap governed by the net active N, in full agreement with experimental results. Our results for the electronic structure and the frequency of the local vibrational mode of the Si-N split interstitial provide a guide for further experiments on mutual passivation effects in highly mismatched semiconductor alloys.

Our calculations are based on density-functional theory (DFT) within the local density approximation (LDA) and pseudopotentials as implemented in the VASP code [12–15]. We use a plane-wave basis set with a cutoff of 400 eV. GaAsN alloys with different N concentrations were simulated by supercells containing 64, 128, or 216 atoms, in which one As was replaced by one N; this corresponds to a N content of 3.1%, 1.6%, or 0.9%, respectively. Integrations over the Brillouin zone were performed using a \(2 \times 2 \times 2\) grid of Monkhorst-Pack special \(k\) points for the 64-atom supercell, and \(1 \times 1 \times 1\) grids for 128- and 216-atom supercells. These calculations allow us to analyze trends with band gap in alloys with different nitrogen concentrations. In order to address the DFT-LDA underestimation of the band gap, we performed calculations with two different pseudopotentials: one in which the Ga 3\textit{d} electrons are explicitly included as valence states, the other with Ga\textsubscript{p} pseudopotentials: one in which the Ga\textsubscript{p} electrons frozen in the core. The two situations produce very similar results for structure and energetics, but the “\textit{d} in the core” potential results in a band gap that is larger by 0.15 eV.

The behavior of Si in GaAs is well established. Si predominantly occupies Ga sites and is a hydrogenic shallow donor; i.e., its extra valence electron is loosely bound and can be thermally excited to the GaAs conduction band. In GaAsN, the formation energy of Si\textsubscript{Ga}\textsubscript{As}\textsubscript{N} is given by

\[
E_b^{\text{(Si\textsubscript{Ga}\textsubscript{As}\textsubscript{N})}} = E_{\text{tot}}^{\text{(Si\textsubscript{Ga}\textsubscript{As})}} - E_{\text{tot}}^{\text{(GaAsN)}} - \mu_{\text{Si}} + \mu_{\text{Ga}} + E_F,
\]

where \(E_{\text{tot}}^{\text{(Si\textsubscript{Ga}\textsubscript{As})}}\) is the total energy of a GaAsN supercell with one Ga replaced by one Si atom, \(E_{\text{tot}}^{\text{(GaAsN)}}\) is the total energy of GaAsN in the same supercell, and \(\mu_{\text{Si}}\) and \(\mu_{\text{Ga}}\) are the Si and Ga chemical potentials. For Si, \(\mu_{\text{Si}}\) is simply the total energy per atom in a Si crystal, \(E_{\text{tot}}^{\text{(Si)}}\). \(\mu_{\text{Ga}}\), on the other hand, can vary from \(\mu_{\text{Ga}} = E_{\text{tot}}^{\text{(Ga)}}\) (the total energy per atom in a Ga crystal) under Ga-rich conditions to \(\mu_{\text{Ga}} = E_{\text{tot}}^{\text{(Ga)}} + \Delta H_1^{\text{(GaAsN)}}\) (Ga-poor conditions), where \(\Delta H_1^{\text{(GaAsN)}}\) is the calculated formation enthalpy of the GaAsN alloys [16]. \(E_F\) is the Fermi-level position, which is commonly referenced to the valence-band maximum. Our calculated formation energy is shown in Fig. 2.

The binding energy of Si\textsubscript{Ga}\textsubscript{As}\textsubscript{N} with respect to the isolated species Si\textsubscript{Ga} and N\textsubscript{As} is defined as

\[
E_b = E^{\text{(Si\textsubscript{Ga})}} + E^{\text{(N\textsubscript{As})}} - E^{\text{(Si\textsubscript{Ga}\textsubscript{As}\textsubscript{N})}},
\]

resulting in a positive \(E_b\) if the complex is lower in energy than the isolated species. If we assume both Si\textsubscript{Ga} and Si\textsubscript{Ga}\textsubscript{As}\textsubscript{N} to be in the \textit{positive} charge state, then the calculated binding energy is actually negative: the configuration where Si\textsubscript{Ga}\textsuperscript{+} is far away from N\textsubscript{As} has an energy that is lower than that of Si\textsubscript{Ga}\textsubscript{As}\textsubscript{N} by 0.04 eV. This value differs from the result of Li \textit{et al.} [11], who found a binding energy of 0.26 eV. Li \textit{et al.} [11] assumed that Si\textsubscript{Ga} and Si\textsubscript{Ga}\textsubscript{As}\textsubscript{N} would be in the \textit{neutral} charge state; for the shallow donor Si\textsubscript{Ga} this implies placing an electron in a shallow level close to the conduction-band minimum (CBM). Li \textit{et al.} [11] used the value of the GaAs CBM in their derivation. While it is true that for purposes of defining the binding energy Si\textsubscript{Ga} should be far from the N\textsubscript{As}, it should be clear that in an alloy such as GaAsN the CBM is shifted down throughout the material. Therefore the formation energy of Si\textsubscript{Ga}\textsuperscript{+} should be determined using the GaAsN CBM, which is considerably lower than that of GaAs. If we strictly follow the procedure of Li \textit{et al.}, we find \(E_b = 0.27\) eV, virtually identical to their value; however, if we properly reference the formation energy of the neutral charge state to the CBM of the GaAsN alloy, the calculated binding energy is lowered to 0.11 eV. This low value (along with the negative value we obtained for the binding energy of

\[
\begin{align*}
\text{Si}\textsubscript{Ga}\textsuperscript{+} + \text{N}\textsubscript{As} & \rightarrow \text{Si}\textsubscript{Ga}\textsubscript{As}\textsubscript{N} \\
\text{Si}\textsubscript{Ga}\textsubscript{As}\textsubscript{N} & \rightarrow \text{Si}\textsubscript{Ga}\textsuperscript{+} + \text{N}\textsubscript{As}
\end{align*}
\]

FIG. 2. Formation energy as a function of Fermi-level position for Si\textsubscript{Ga}\textsubscript{As}\textsubscript{N} and (Si-N)\textsubscript{As} in GaAsN, under Ga-rich conditions. The Fermi level varies from 0 to 1.25 eV, which corresponds to the band gap of GaAsN alloys with a N concentration of about 1% [7].
the positive charge state) indicates that there is only a very weak driving force for $\text{Si}_{\text{Ga}}$ and $\text{N}_{\text{As}}$ to form $\text{Si}_{\text{Ga}}\text{-N}_{\text{As}}$ pairs. The assumption in previous work [7–9] that $\text{Si}_{\text{Ga}}$ and $\text{N}_{\text{As}}$ would form a bond that is significantly stronger than the $\text{Ga}_{\text{Ga}}\text{-N}_{\text{As}}$ bond is clearly unjustified.

A much more likely bonding configuration is found in our proposed $(\text{Si-N})_{\text{As}}$ split-interstitial complex. The formation energy of $(\text{Si-N})_{\text{As}}$ in charge state $q$ is given by

$$E^q[(\text{Si-N})_{\text{As}}] = E_{\text{tot}}[(\text{Si-N})_{\text{As}}^q] - E_{\text{tot}}(\text{GaAsN}) - \mu_{\text{Si}} + qE_F.$$  

(3)

Figure 2 shows that the split interstitial can occur in the neutral and negative charge states, with a transition level $\varepsilon(0/-)$ at 0.89 eV above the VBM. $(\text{Si-N})_{\text{As}}$ thus acts as a deep acceptor and is stable in the negative charge state for $E_F > 0.89$ eV.

In the $(\text{Si-N})_{\text{As}}$ configuration, Si and N are both threefold coordinated in planar geometries: Si is bonded to N and two Ga atoms, and N is bonded to Si and two other Ga atoms; the surrounding Ga atoms are all fourfold coordinated as shown in Fig. 1(b). In the neutral charge state the Si-N bond length is 1.65 Å. The N-Ga and Si-Ga bond lengths are 1.89 and 2.33 Å, and these Ga atoms are displaced outward from their nominal lattice sites by distances corresponding to 1.0% and 8.5% of the equilibrium Ga-As bond length. This is a small perturbation when compared to inward displacements of 16% for the Ga atoms surrounding an isolated N in GaAsN alloys, or 12% for the three Ga atoms surrounding the N in the $\text{Si}_{\text{Ga}}\text{-N}_{\text{As}}$ pair. Note that we did not impose any symmetry constraints in the relaxation of the Si-N configurations.

The electronic structure of the $(\text{Si-N})_{\text{As}}$ split interstitial can be understood based on electron counting: the removal of an As atom leaves four Ga dangling bonds with a total of three electrons. The $(\text{Si-N})_{\text{As}}$ pair contributes nine valence electrons, leading to a combined total of 12 electrons. Eight of these are accommodated in two N-Ga and two Si-Ga bonds. Two electrons are accommodated in a Si-N $\pi$ bond, and we are left with two electrons. The $p_z$ orbitals on N and Si are oriented in mutually perpendicular directions, preventing the formation of a $\sigma$ bond. However, they still combine into a doubly occupied bonding state located near the VBM, and an empty antibonding state at 0.95 eV above the VBM. Since N is more electronegative than Si, the bonding state has more nitrogen character and the antibonding state more Si character, as shown in Fig. 3. Moreover, we observe that the band gap of GaAs is restored upon formation of the $(\text{Si-N})_{\text{As}}$ split interstitial. In our supercell, the next available Kohn-Sham state above the antibonding state is in the GaAs conduction band. Therefore the formation of the $(\text{Si-N})_{\text{As}}$ complex removes the effect of N on the band gap, but at the expense of forming a deep level.

The antibonding state at 0.95 eV (averaged over the special $k$ points) above the VBM can in principle accept up to two electrons, corresponding to negative (−) and doubly negative (2−) charge states of $(\text{Si-N})_{\text{As}}$. We find the $\varepsilon(-/2-)$ transition level at 1.25 eV above the VBM, which places it above the CBM of the GaAsN alloy. In the −2− charge state we observe a small increase in the Si-N bond length (1.68 Å) compared to the value in the neutral configuration (1.65 Å). The Ga atoms are displaced outward from their nominal lattice sites by 0.8% and 6.8% of the equilibrium Ga-As bond length.

Figure 2 also shows that the formation energy of $(\text{Si-N})_{\text{As}}$ is lower than that of the $\text{Si}_{\text{Ga}}\text{-N}_{\text{As}}$ pair for Fermi-level positions above 0.6 eV. Even under extreme Ga-poor conditions the formation energy of $(\text{Si-N})_{\text{As}}$ remains lower than that of $\text{Si}_{\text{Ga}}^+\text{-N}_{\text{As}}$ when $E_F$ is near the CBM (as is the case in the experiments [8]). In this case the formation energy of negatively charged $(\text{Si-N})_{\text{As}}$ is 0.4 eV lower than that of positively charged $\text{Si}_{\text{Ga}}^+\text{-N}_{\text{As}}$. $(\text{Si-N})_{\text{As}}$ acts as a compensating acceptor in GaAsN, and charge neutrality requires that the net electron concentration is the difference between the $\text{Si}_{\text{Ga}}^+$ and $(\text{Si-N})_{\text{As}}^-$ concentrations. Since the electron concentration is much smaller than the total Si concentration after annealing at 800 °C or above [8], we conclude that the final concentrations of $\text{Si}_{\text{Ga}}$ and $(\text{Si-N})_{\text{As}}$ must be very close.

The formation of $(\text{Si-N})_{\text{As}}$ split interstitials can also explain the peak at ∼0.8 eV in the photoluminescence spectra [7,9]. The exciting photons create electron-hole pairs. In the presence of holes in the valence band, negatively charged $(\text{Si-N})_{\text{As}}$ complexes can convert to neutral by emitting a photon at 0.85 eV, as shown in Fig. 3(c). We note that the position of this peak is essentially independent of the nitrogen concentration, and also not sensitive to the DFT-LDA underestimation of the gap, as checked by performing calculations with different pseudopotentials that produce different gaps.

Now we consider why the formation of $(\text{Si-N})_{\text{As}}$ in Si-doped GaAsN requires annealing at temperatures above 800 °C. Dilute GaAsN alloys are typically grown at relatively low temperatures ($T < 500^\circ \text{C}$) to prevent N segregation. Si can be introduced during this low-temperature growth or by ion implantation; either way, the resulting Si$_{\text{Ga}}$ donors are unable to find their lowest-energy configu-
Our results indicate that the formation of Ge-doped GaAsN will be published elsewhere. Si, e.g., energies of these complexes to be significantly higher stretch frequency of Si-N stretch mode of Si-NAs splits interstitials. This process involves the emission of a Ga vacancy, but since Ga vacancies are mobile at these temperatures their concentration will rapidly return to the equilibrium concentration.

Germanium is also an important candidate for n-type doping in dilute GaAsN alloys. We find that Ge also combines with N into stable (Ge-N)As split interstitials that have lower formation energy than GeGaN pairs. The formation of (Ge-N)As also explains the mutual passivation between Ge and N in Ge-doped GaAsN alloys as observed by Wu et al. [8]. A detailed discussion of the results for Ge-doped GaAsN will be published elsewhere. Our results indicate that the formation of (Si-N)As or (Ge-N)As split interstitials is also likely to occur in other III–V based dilute nitride alloys, such as InGaAsN, GaPN, and InGaPN alloys.

In addition, our model nicely explains why column-VI dopants (such as S and Se) behave differently. In this case, (S-N)As and (Se-N)As split interstitials are less stable than the isolated SAs or SeAs donor configurations. The reason is that the column-VI donors have two more electrons than column-IV donors, and hence the antibonding state formed from p, orbitals is occupied by two electrons in the (S-N)As or (Se-N)As split interstitial. This causes the formation energies of these complexes to be significantly higher [e.g., (S-N)As is more than 1 eV higher in energy than isolated SeAs], rendering them unstable with respect to the isolated species. Therefore S- or Se-doped GaAsN does not suffer from the mutual passivation effect.

Finally, we also calculated the local vibrational mode associated with the (Si-N)As split interstitial. The calculations were performed by displacing the Si and N atoms in the three Cartesian directions and diagonalizing the force-constant matrix as described in Ref. [19]. Since the masses of N and Si are much smaller than the mass of the Ga atoms, we find that considering the displacements of Si and N alone is a good approximation. The calculated frequency of the Si-N stretch mode of (Si-N)As is 935 cm$^{-1}$ in the neutral charge state and 884 cm$^{-1}$ in the negative charge state. These frequencies are much higher than the Si-N stretch frequency of 563 cm$^{-1}$ associated with the SiGaN pair. These predicted vibrational frequencies can therefore serve as a guide for experimental identification of the Si-N complex associated with the mutual passivation effect.

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