

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 ($\text{Si}_{\text{Ga}}\text{-N}_{\text{As}}$) [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 $[(\text{Si-N})_{\text{As}}]$, with a significantly lower formation energy than that of the $\text{Si}_{\text{Ga}}\text{-N}_{\text{As}}$ pair in *n*-type GaAs and dilute GaAsN alloys. The formation of $(\text{Si-N})_{\text{As}}$ 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 $\text{GaAs}_{1-x}\text{N}_x$ 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 $\text{GaAs}_{1-x}\text{N}_x$ alloys. While the physics of *n*-type and *p*-type doping in the parent compounds GaAs and GaN is well established, doping in $\text{GaAs}_{1-x}\text{N}_x$ is much less explored. Recent reports indicate that the interaction between extrinsic dopants and N in $\text{GaAs}_{1-x}\text{N}_x$ alloys can lead to entirely new phenomena [7–10]. Yu *et al.* [7] reported that when $\text{GaAs}_{1-x}\text{N}_x$ 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 $\text{GaAs}_{1-x}\text{N}_x$ [9]. It was postulated that substitutional Si_{Ga} and Ge_{Ga} form strong bonds with N_{As} and lead to deep donor levels, eliminating the shallow-donor character of Si and Ge in $\text{GaAs}_{1-x}\text{N}_x$ alloys. On the other hand, S_{As} and Se_{As} are (at best) second-nearest neighbors of N_{As} and not

directly bonded to N_{As} ; therefore they would not suffer from the passivation effect [7–9].

First-principles calculations by Li *et al.* suggested that the $\text{Si}_{\text{Ga}}\text{-N}_{\text{As}}$ 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 $\text{Si}_{\text{Ga}}\text{-N}_{\text{As}}$ 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 $\text{Si}_{\text{Ga}}\text{-N}_{\text{As}}$ pairs at temperatures above 800 °C. At these temperatures, we estimate that less than 40% of the Si atoms would be bonded to N_{As} in $\text{Si}_{\text{Ga}}\text{-N}_{\text{As}}$ 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 $\text{Si}_{\text{Ga}}\text{-N}_{\text{As}}$ 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

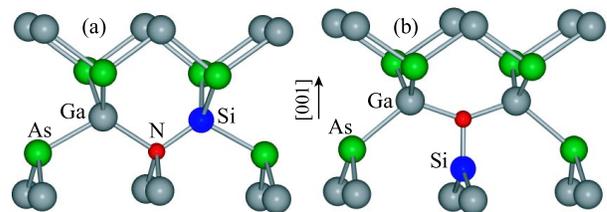


FIG. 1 (color online). Local structure of (a) $(\text{Si}_{\text{Ga}}\text{-N}_{\text{As}})^+$ and (b) $(\text{Si-N})_{\text{As}}^-$. In the $\text{Si}_{\text{Ga}}\text{-N}_{\text{As}}$ configuration, Si_{Ga} is a nearest neighbor of N_{As} ; in the $(\text{Si-N})_{\text{As}}$ configuration, Si and N share an As site.

in a more dramatic way. Based on first-principles density-functional calculations we find that Si combines with N into stable $(\text{Si-N})_{\text{As}}$ split interstitials that act as compensating centers in n -type GaAsN. The $(\text{Si-N})_{\text{As}}$ split interstitial is a *deep acceptor* with a formation energy that is significantly lower than that of $\text{Si}_{\text{Ga}}\text{-N}_{\text{As}}$ in 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 $(\text{Si-N})_{\text{As}}$ 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 $(\text{Si-N})_{\text{As}}$ split interstitials in annealed Si-doped $\text{GaAs}_{1-x}\text{N}_x$ 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 3d electrons are explicitly included as valence states, the other with Ga 3d electrons frozen in the core. The two situations produce very similar results for structure and energetics, but the “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_{Ga}^+ is given by

$$E^f(\text{Si}_{\text{Ga}}^+) = E_{\text{tot}}(\text{Si}_{\text{Ga}}^+) - E_{\text{tot}}(\text{GaAsN}) - \mu_{\text{Si}} + \mu_{\text{Ga}} + E_F, \quad (1)$$

where $E_{\text{tot}}(\text{Si}_{\text{Ga}}^+)$ 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 μ_{Si} and μ_{Ga} are the Si and Ga chemical potentials. For Si, μ_{Si} is simply the total energy per atom in a Si crystal, $E_{\text{tot}}(\text{Si})$. μ_{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 $\mu_{\text{Ga}} = E_{\text{tot}}(\text{Ga}) + \Delta H_f(\text{GaAsN})$ (Ga-poor conditions), where $\Delta H_f(\text{GaAsN})$ 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 $\text{Si}_{\text{Ga}}\text{-N}_{\text{As}}$ with respect to the isolated species Si_{Ga} and N_{As} is defined as

$$E_b = E^f(\text{Si}_{\text{Ga}}) + E^f(\text{N}_{\text{As}}) - E^f(\text{Si}_{\text{Ga}}\text{-N}_{\text{As}}), \quad (2)$$

resulting in a positive E_b if the complex is lower in energy than the isolated species. If we assume both Si_{Ga} and $\text{Si}_{\text{Ga}}\text{-N}_{\text{As}}$ to be in the *positive* charge state, then the calculated binding energy is actually negative: the configuration where Si_{Ga}^+ is far away from N_{As} has an energy that is lower than that of $\text{Si}_{\text{Ga}}\text{-N}_{\text{As}}$ by 0.04 eV. This value differs from the result of Li *et al.* [11], who found a binding energy of 0.26 eV. Li *et al.* [11] assumed that Si_{Ga} and $\text{Si}_{\text{Ga}}\text{-N}_{\text{As}}$ would be in the *neutral* charge state; for the shallow donor Si_{Ga} this implies placing an electron in a shallow level close to the conduction-band minimum (CBM). Li *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_{Ga} should be far from the N_{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_{Ga}^0 should be determined using the GaAsN CBM, which is considerably lower than that of GaAs. If we strictly follow the procedure of Li *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

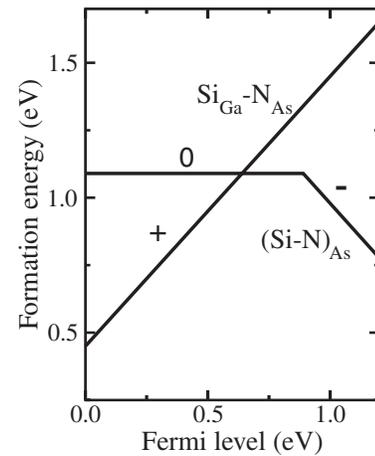


FIG. 2. Formation energy as a function of Fermi-level position for $\text{Si}_{\text{Ga}}\text{-N}_{\text{As}}$ and $(\text{Si-N})_{\text{As}}$ in GaAsN, under Ga-rich conditions. The Fermi level varies from 0 to 1.25 eV, which corresponds to the band gap of GaAsN alloys with a N concentration of about 1% [7].

the positive charge state) indicates that there is only a very weak driving force for Si_{Ga} and N_{As} to form $\text{Si}_{\text{Ga}}\text{-N}_{\text{As}}$ pairs. The assumption in previous work [7–9] that Si_{Ga} and N_{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

$$E^J[(\text{Si-N})_{\text{As}}^q] = E_{\text{tot}}[(\text{Si-N})_{\text{As}}^q] - E_{\text{tot}}(\text{GaAsN}) - \mu_{\text{Si}} + qE_F. \quad (3)$$

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 σ 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 π 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

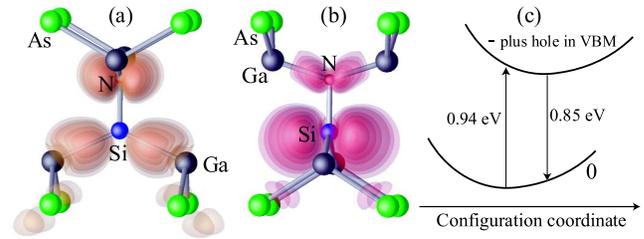


FIG. 3 (color online). Charge density isosurfaces of the (a) bonding and (b) antibonding states associated with $(\text{Si-N})_{\text{As}}$. The structure in (b) has been rotated with respect to (a) to better visualize the localization of the states. (c) Calculated configuration coordinate diagram for $(\text{Si-N})_{\text{As}}$ indicating energies at which absorption and luminescence occur.

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 $-$ and $2-$ charge states 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 Si_{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 Si_{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 ($T < 500$ °C) to prevent N segregation. Si can be introduced during this low-temperature growth or by ion implantation; either way, the resulting Si_{Ga} donors are unable to find their lowest-energy configu-

ration [in $(\text{Si-N})_{\text{As}}$ complexes] during this nonequilibrium incorporation process. Annealing at temperatures above 800°C allows Si atoms to diffuse (mediated by Ga vacancies [17]) and find their equilibrium configuration, while the N atoms are locked into the lattice since their diffusion requires much higher temperatures [18]. At 800°C the mean free path of Si is long enough for Si atoms to encounter N atoms [7–9]. Si_{Ga} then combines with N_{As} into stable $(\text{Si-N})_{\text{As}}$ split 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 $(\text{Ge-N})_{\text{As}}$ split interstitials that have lower formation energy than $\text{Ge}_{\text{Ga}}\text{-N}_{\text{As}}$ pairs. The formation of $(\text{Ge-N})_{\text{As}}$ 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 $(\text{Si-N})_{\text{As}}$ or $(\text{Ge-N})_{\text{As}}$ 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, $(\text{S-N})_{\text{As}}$ and $(\text{Se-N})_{\text{As}}$ split interstitials are less stable than the isolated S_{As} or Se_{As} 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_z orbitals is occupied by two electrons in the $(\text{S-N})_{\text{As}}$ or $(\text{Se-N})_{\text{As}}$ split interstitial. This causes the formation energies of these complexes to be significantly higher [e.g., $(\text{Se-N})_{\text{As}}$ is more than 1 eV higher in energy than isolated Se_{As}], 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 $(\text{Si-N})_{\text{As}}$ 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 $(\text{Si-N})_{\text{As}}$ 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 $\text{Si}_{\text{Ga}}^+\text{-N}_{\text{As}}$ pair. These predicted vibrational frequencies can therefore serve as a guide for experimental identifica-

tion of the Si-N complex associated with the mutual passivation effect.

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- [1] M. Weyers *et al.*, Jpn. J. Appl. Phys., Part 2 **31**, L853 (1992).
 - [2] J. Neugebauer and C.G. Van de Walle, Phys. Rev. B **51**, 10 568 (1995).
 - [3] S.-H. Wei and A. Zunger, Phys. Rev. Lett. **76**, 664 (1996).
 - [4] W. Shan *et al.*, Phys. Rev. Lett. **82**, 1221 (1999).
 - [5] J.C. Woolley, in *Compound Semiconductors*, edited by R.K. Willardson and H.L. Goering (Reinhold, New York, 1962), p. 3.
 - [6] Special issue on III-N-V Semiconductor Alloys, edited by J.W. Ager III and W. Walukiewicz [Semicond. Sci. Technol. **17**, 8 (2002)].
 - [7] K.M. Yu, W. Walukiewicz, J. Wu, D.E. Mars, D.R. Chamberlin, M.A. Scarpula, O.D. Dubon, and J.F. Geisz, Nat. Mater. **1**, 185 (2002).
 - [8] J. Wu, K.M. Yu, W. Walukiewicz, G. He, E.E. Haller, D.E. Mars, and D.R. Chamberlin, Phys. Rev. B **68**, 195202 (2003).
 - [9] K.M. Yu, W. Walukiewicz, J. Wu, W. Shan, J.W. Beeman, M.A. Scarpula, O.D. Dubon, M.C. Ridgway, D.E. Mars, and D.R. Chamberlin, Appl. Phys. Lett. **83**, 2844 (2003).
 - [10] Y.G. Hong, A. Nishikawa, and C.W. Tu, Appl. Phys. Lett. **83**, 5446 (2003).
 - [11] J. Li, P. Carrier, and S.-H. Wei, S.-S. Li, and J.-B. Xia, Phys. Rev. Lett. **96**, 035505 (2006).
 - [12] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965).
 - [13] P.E. Blöchl, Phys. Rev. B **50**, 17953 (1994); G. Kresse and J. Joubert, Phys. Rev. B **59**, 1758 (1999).
 - [14] D. Vanderbilt, Phys. Rev. B **32**, 8412 (1985).
 - [15] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11 169 (1996); G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
 - [16] C.G. Van de Walle and J. Neugebauer, J. Appl. Phys. **95**, 3851 (2004).
 - [17] A. Janotti, S.-H. Wei, S.B. Zhang, and S. Kurtz, and C.G. Van de Walle, Phys. Rev. B **67**, 161201 (2003).
 - [18] G. Bosker, N.A. Stolwijk, J. Thordson, U. Sodervall, and T.G. Andersson, Phys. Rev. Lett. **81**, 3443 (1998).
 - [19] A. Janotti, S.B. Zhang, and S.-H. Wei, Phys. Rev. Lett. **88**, 125506 (2002).