

Influence of hydrostatic pressure on cation vacancies in GaN, AlN, and GaAs

I. Gorczyca

High Pressure Research Center, Polish Academy of Sciences, Warsaw, Poland

N. E. Christensen and A. Svane

Institute of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark

(Received 7 March 2002; revised manuscript received 10 June 2002; published 26 August 2002)

The effects of hydrostatic pressure on the formation energy and electronic level positions of cation vacancies in GaN, AlN, and GaAs are examined by means of *ab initio* calculations using a supercell approach in connection with the full-potential linear-muffin-tin-orbital method. Atomic relaxations are fully taken into account. Substantial differences are revealed in the pressure behavior of the defect level positions and formation energies for the cation vacancies in the nitride compounds and in GaAs. Additionally, the arsenic antisite in GaAs is examined, also exhibiting pressure response different from that of the vacancies. The pressure effect is strong for the vacancy and the antisite in GaAs, but for similar defects in the III-V nitrides it is rather weak.

DOI: 10.1103/PhysRevB.66.075210

PACS number(s): 71.55.Eq, 71.55.-i

I. INTRODUCTION

The electronic quality of a semiconductor is largely determined by the nature and number of its native defects. In the present paper we study the cation vacancies that are the most stable native defects of technological interest in some tetrahedral semiconductors of *n* type.¹ The main goal of the paper is to find the pressure and defect charge dependence of the formation energies of the studied defects. Proper understanding of the formation of defects allows for tuning the material properties by controlling the doping. The work was also motivated by the study performed by Bonapasta and Giannozzi² on the Ga vacancy and As-antisite defects in GaAs and InGaAs. They showed that the formation of vacancies and antisites is related to a *fine interplay* between changes of lattice constant, strain, and charges on the defect, and that in the case of GaAs or InGaAs their results have applications in the *defect engineering*, where doping characteristics are tuned by application of pressure. The present work examines whether the strong effects of pressure and defect charge on formation energies found for GaAs are also present in the III-V nitrides. The nitrides exhibit unique properties such as large band gaps, strong bonds, and high thermal conductivity, rendering these compounds very interesting from the point of view of application. The “unusual” behavior of the nitrides have earlier been mentioned in Refs. 3 and 4, and references given therein. In the present work we compare the formation energies, the electronic energy levels, and the behavior under pressure of the cation vacancies in GaAs, which is an example of a well-studied III-V compound semiconductor, to the same quantities in the nitrides AlN and GaN. To show more clearly which features are typical for Ga vacancies, we perform similar calculations for the arsenic antisite in GaAs, which is a complementary defect to the cation vacancy. Cation vacancies are deep acceptors while the As antisite is a deep donor. Furthermore, both cation vacancies and As antisite are favored by the presence of an excess of As atoms, i.e., under As-rich growth conditions.

The analysis of the effects of hydrostatic pressure on the level positions and the formation energies of cation vacan-

cies and the arsenic antisite, taking into account different charge states of the considered defects, is made by *ab initio* supercell calculations using the full-potential linear-muffin-tin-orbital (LMTO) method. The effects of lattice relaxation near the defects and their influence on the defect level positions in the energy gap are also discussed. Although the main features of cation vacancies (formation energies and energy-level positions) are similar in all three compounds, we find substantial differences when comparing the pressure response of these defects in the nitride compounds on one hand and in GaAs on the other. This difference, however, is mainly due to the difference in rigidity of the GaAs and nitride lattices.

In Sec. II, the calculational method is described, and in Sec. III results for the selected native defects are presented. Section IV contains a brief summary.

II. METHOD

To study the lattice relaxation effects in the neighborhood of defects, the full nonspherical shapes of potentials and charge distributions are taken into account. We do this by combining the supercell approach with the full-potential version⁵ of the linear-muffin-tin-orbital method.⁶ Calculations were performed using 32-atom supercells, and we have used the LMTO basis sets including partial waves of *s*, *p*, and *d* character on each atomic site, giving a total of 44 LMTO orbitals per formula unit. The *k* space integrations used 512 *k* points in the Brillouin zone and convergence tests were made with 1728 *k* points. All (nonoverlapping) muffin-tin spheres are chosen to have the same size. As usual, in open structures, empty spheres (muffin-tin spheres without nuclear charge) were inserted in the interstitial regions to improve the packing fraction.⁷ The local-density approximation (LDA) (Ref. 8) to the density-functional theory was used, and we applied the Perdew-Zunger⁹ parametrization of the Ceperley-Alder exchange-correlation.¹⁰

The finite size of the supercell implies that the impurity states appear as bands of nonzero widths. We can estimate the impurity levels in the band gap as the center of gravity of

the impurity band. This is determined by means of the density-of-states (DOS) functions. The large number of k points is, in particular, necessary to obtain accurate DOS functions. As an alternative method we used the total-energy calculations to derive the defect levels as the Fermi energies where the defect charges change by one unit. The defect calculations were performed for the cubic (zinc-blende) phase for three compounds: GaAs, GaN, and AlN. The two nitride materials also exist in the hexagonal wurtzite structure. However, the zinc-blende and wurtzite structures are both tetrahedrally coordinated, which means that the nearest-neighbor shells are equivalent in both cases. Therefore, we believe that our results for the cubic phase also describe the situation quite well in the hexagonal phase. This is also supported by earlier *ab initio* studies^{1,3} that show that the formation energies and electronic structures of defects are very similar in the two phases, and the energy-level positions were practically the same.

To check the stability of defects created under pressure, we calculated the formation energies for different values of the hydrostatic pressure. For clarity, we illustrate the method for the case of GaN below, but it can be straightforwardly applied to AlN by replacing Ga with Al, and to GaAs by replacing N by As. The formation energy of a defect in charge state q is defined as

$$E^f(q) = E_{tot}(q) - E_{host} + n_{Ga}\mu_{Ga} + n_N\mu_N - n_d\mu_d - q\mu_e, \quad (1)$$

where E_{tot} is the total energy of the defect supercell, E_{host} is the total energy of the host supercell, and n_{Ga} and n_N are the numbers of Ga and N atoms substituted by the defect, μ_{Ga} and μ_N being their chemical potentials. Similarly, n_d and μ_d are the number of defect atoms and their chemical potential, respectively. Finally, μ_e corresponds to the electron chemical potential, i.e., the Fermi-level position in the gap. Reference 4 contains a detailed description of the method, the results for neutral defects in the nitrides, as well as the values used for the chemical potentials. These were also used in the present work, and we assumed that the pressure dependence of the μ values could be neglected. For example, the pressure variation of μ_{Ga} under N-rich conditions can be estimated in the following way: With $\mu_N = (1/2)E(N_2)$ assumed to be independent of pressure, the Ga chemical potential is

$$\mu_{Ga}(P) = E(\text{GaN}) - \mu_N \approx \frac{1}{2} \frac{V}{B} P^2 + \mu_{Ga}(0), \quad (2)$$

where $V = 22.78 \text{ \AA}^3/\text{f.u.}$ is the specific volume and $B = 200 \text{ GPa}$ is the bulk modulus.³ At a pressure $P = 10 \text{ GPa}$, this gives $\mu_{Ga}(P) - \mu_{Ga}(0) \approx 0.035 \text{ eV}$.

III. RESULTS

In Table I, the change in defect geometry with charge state and with hydrostatic pressure is reported for the cation vacancies in the three compounds studied. Additionally, the arsenic antisite in GaAs is considered and compared with the vacancies. In all cases, a symmetric outward or inward relaxation around the defect atom is found. The displacement

TABLE I. Defect geometries as a function of charge state for cation vacancies in AlN, GaN, and GaAs, and for the As antisite in GaAs. Displacements of the nearest-neighbor atoms are expressed as a percentage of the ideal bulk bond length. Positive values represent displacements away from the defect center and negative values towards it. In parentheses are given the values of displacements for a hydrostatic pressure equal to 10 GPa.

Charge state	AlN V_{Al}	GaN V_{Ga}	GaAs V_{Ga}	GaAs A_{Ga}
-3	9 (7)	6 (4)	-8 (-10)	
-2	10 (7.5)	7 (4)	-6 (-9)	
-1	10.5 (8)	8 (5)	-4 (-8)	
0	10.5 (8)	8.2 (6.7)	-3 (-7)	4 (4)
1				3 (3)
2				2 (2)

of the nearest-neighbor atoms of the defect with respect to the unrelaxed positions is given as a percentage of the ideal bond length. Positive values represent displacement away from the defect center. In parentheses are given values of the displacements obtained for a compression corresponding to a hydrostatic pressure of 10 GPa.

The Ga vacancy in GaAs introduces a void in the lattice, which causes the nearest-neighbor As atoms to displace *towards* the vacancy. In contrast, for the cation vacancies in AlN and GaN, just the opposite behavior is observed: the nearest-neighbor N atoms move *away from* the defect. This reflects that the nitrides have “small atoms and strong bonds.” In addition, the dependence of the lattice relaxation on the charge state of the defect is different (stronger) for GaAs than for the nitrides. The displacements of the atoms under hydrostatic pressure are systematically smaller than at zero pressure. Again, in the case of the cation vacancy in GaAs, the dependence of the lattice relaxation on pressure seems to be more pronounced.

For the As antisite in GaAs being rather small, outward displacements of the neighboring atoms are observed, caused by the antibonding interactions of the antisite with the neighboring As atoms.¹¹ No dependence on pressure is found.

Due to the band-gap underestimation in density-functional theory or LDA calculations the experimental band-gap values were used in the analysis of ionization levels and formation energy (to extend the range of the chemical potential). The experimental band-gap value for GaAs is 1.5 eV and for zinc-blende GaN about 3.3 eV. However, for zinc-blende AlN the gap is indirect, and the experimental value is not well established. Therefore we used an approximate value of 5 eV based on *GW* calculations.¹²

In Fig. 1 the defect-induced Kohn-Sham levels are shown schematically for the cation vacancies in AlN, GaN, and GaAs, and for the As antisite in GaAs. The energies are obtained from the DOS functions as the centers of gravity of the impurity bands. The energies are given in eV above the valence-band maximum (VBM). Their pressure coefficients are given in units of meV/GPa in parentheses. In all three compounds the V_{cat} creates a set of states in the lower part of the band gap; the neutral state is occupied by three electrons

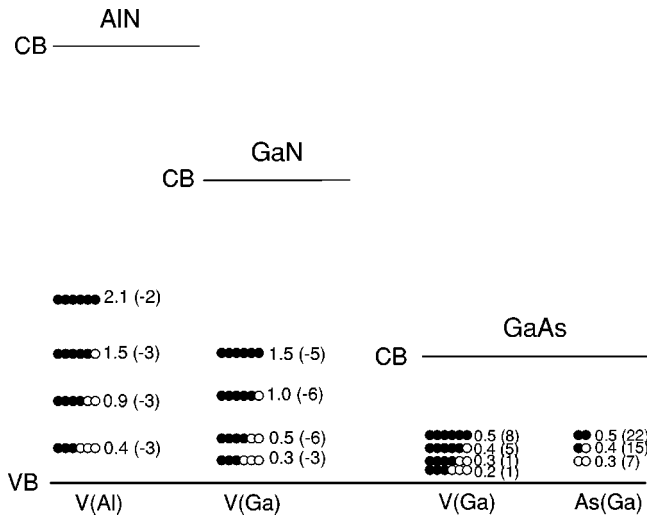


FIG. 1. Schematic representation of the defect-induced electronic states in zinc blende AlN, GaN, and GaAs. Energies (in eV) of the levels above the VBM were obtained from the centers of gravity of the impurity density-of-states functions. The numbers in parantheses are the calculated pressure coefficients (in meV/GPa) for the level energies. Filled and open circles denote electrons and holes, respectively.

and the higher, negatively charged states are filled with up to three more electrons. V_{cat} , being a triple acceptor and lying low in the band gap, is made up of states that have valence-band character. We therefore expect that the corrections to the LDA band gap will not significantly affect the positions of these levels.

For the substitutional arsenic antisite in GaAs, the impurity level in the gap for the neutral charge state is doubly occupied. It lies ≈ 0.5 eV above the VBM. The positively charged states (As^+ and As^{2+}) lie slightly below.

The properties of vacancies in GaAs and the nitrides differ mainly with respect to their pressure dependence. In AlN and GaN, all the pressure coefficients of the energy levels are small and negative without special dependence on the level position/charge state. In contrast, in GaAs the pressure coefficients of the cation vacancy states are positive and it appears to be a rule that for states lying higher in the gap the pressure coefficients also have higher values. The energy-level positions for the As antisite and Ga vacancy in GaAs are very similar, but the pressure coefficients for the antisite levels are larger. The charge dependence follows the rule mentioned above.

Figures 2–5 show the calculated defect formation energies of the cation vacancies and the As antisite defect assuming the most favorable growth conditions for these defects, i.e., the anion-rich limit. The formation energies are plotted as a function of the Fermi energy, for two values of the hydrostatic pressure, $P=0$ and 10 GPa. The changes in slope of the lines represent changes in the charge state of the defect, while the corresponding transition levels are marked with vertical lines. The differences between these energy levels and those of Fig. 1 are mainly due to the uncertainty in location of the level in the density of impurity states (as used for the data in Fig. 1). Pronounced differences are particu-

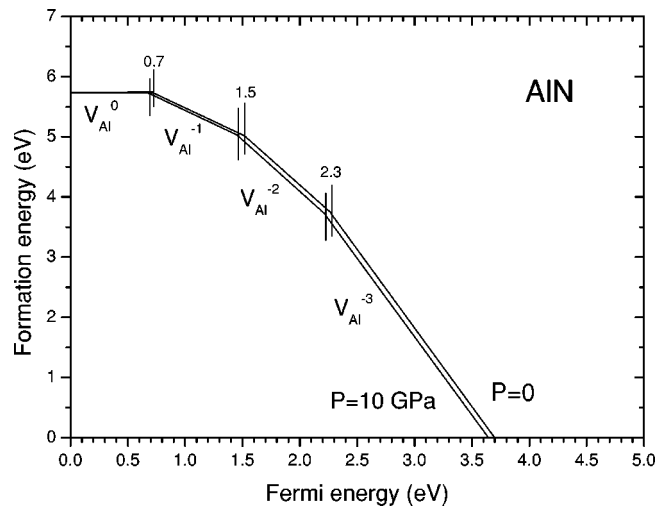


FIG. 2. Formation energies as a function of the Fermi level for the Al vacancy in AlN under nitrogen-rich condition for two values of the hydrostatic pressure, 0 and 10 GPa. $E_F=0$ corresponds to the valence-band maximum. The vertical lines represent transition levels, i.e., Fermi energies where the defect charge changes by one unit.

larly seen for GaAs. The width of the impurity band for Ga vacancy in GaAs is about 0.7 eV. To check how our results depend on the size of the supercell we performed the calculations for a 64-atom cell for two cases: GaAs : $V(Ga)$ in the neutral and in the (-1) charge state. Comparing with the results obtained for a 32-atom cell, we found in the case of the 64-atom cell an upward shift of the $V(Ga)$ defect level positions in both charge states of up to 0.1 eV as calculated from DOS, and a positive shift of the $(-1/0)$ transition level as calculated from the total energies of about 0.03 eV only. This leads to a better agreement between the two kinds of calculations (DOS and “total energy”). The calculations were performed with 216 k point in the BZ. Using only 64 k points the $(-1/0)$ transition level was found to lie ≈ 0.07 eV higher. Thus, in this case the number of k points

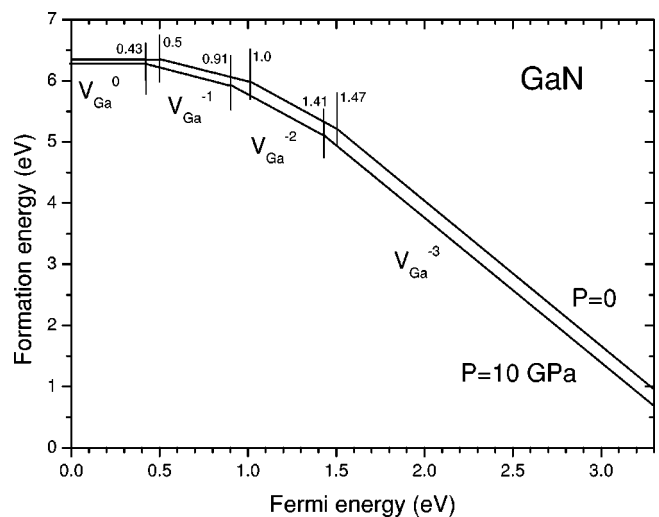


FIG. 3. Same as Fig. 2, but for the Ga vacancy in GaN under nitrogen-rich conditions.

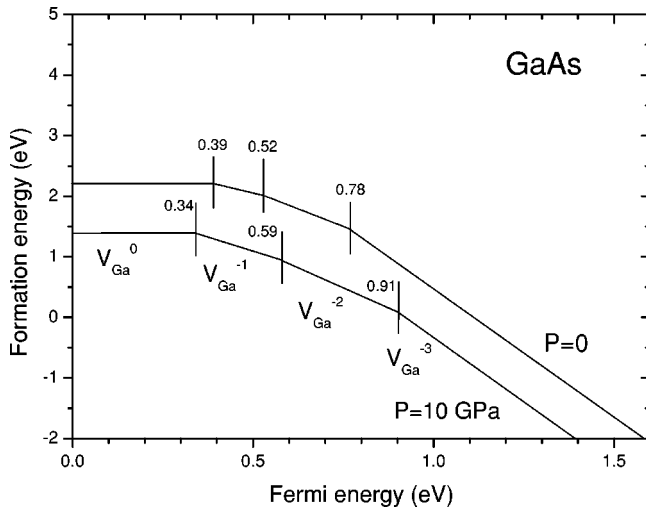


FIG. 4. Same as Fig. 3, but for the Ga vacancy in GaAs under arsenic-rich conditions.

is more crucial than the size of supercell. Summarizing, it follows that the total-energy calculations provide a more accurate (and less cell-size dependent) way of extracting the transition levels than the method where they are obtained from the DOS. Also, a 32-atom cell seems to be large enough to give reasonable positions of the transition levels. The values obtained for the V_{Ga}^{-3} (0.5 eV and 0.78 eV) and for the A_{Ga}^0 (0.45 eV and 0.66 eV) by the two described methods, DOS and total energy, are similar to the values reported in the literature (from 0.57 eV up to 0.7 eV for the vacancy,^{13–15} and from 0.40 eV up to 0.81 eV for the antisite^{11,16–19}). The low value of 0.40 eV in Ref. 19 for the neutral state of As antisite was obtained by the DOS method.

The states of neutral defects in Figs. 2–5 are represented by horizontal lines. With this choice, the corresponding (+1/0) energy level is assigned the value of 0 eV (the VBM).

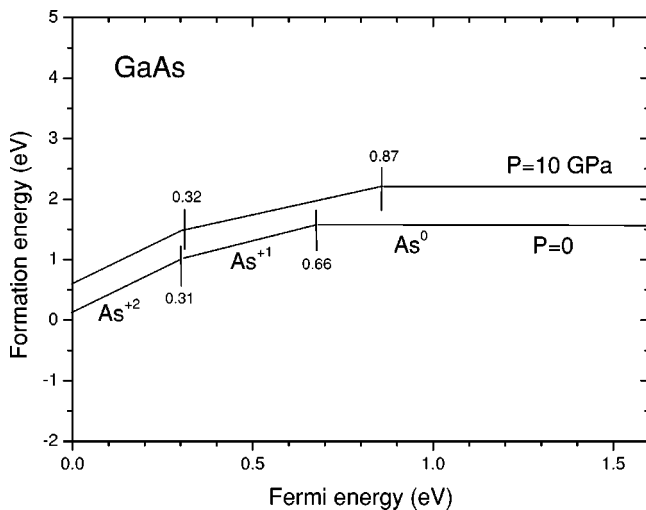


FIG. 5. Same as Fig. 4, but for the As_{Ga} antisite in GaAs under arsenic-rich conditions.

Comparing Figs 2–5 we observe the following:

(1) In n -type materials of all three compounds, where the Fermi level is positioned high in the band gap, the triply negatively charged cation vacancy has a low formation energy, in particular for AlN and GaAs. The behavior of the Al vacancy in AlN is very similar to that of the Ga vacancy in GaN, but due to the larger band gap of AlN, the formation energy of V_{Al}^{-3} becomes significantly lower than that of V_{Ga}^{-3} for high values of the Fermi level.

(2) The formation energy decreases with pressure for all the cation vacancies considered. Quantitative differences are seen in the values of the pressure coefficient and in its dependence on the charge state of the defect. In AlN the dependence on pressure is very weak, while it is somewhat stronger in GaN. In both compounds the pressure effect for different charge states behaves the same way. The pressure coefficients of the formation energies are very small (close to zero in AlN) for the neutral charge state, but increase with the charge of the defect. For V_{Ga}^{-3} , it is -20 meV/GPa. In GaAs, the dependence of the formation energy of the Ga vacancy on pressure is much stronger than in the nitrides (reaching -90 meV/GPa) but with only small dependence on the defect charge.

(3) The formation energy under pressure increases for the As antisite in GaAs. The absolute value of the pressure coefficient is about 60 meV/GPa for the neutral charge state, which is smaller than that of the Ga vacancy in GaAs, but still large. The characteristic feature is that the pressure effects are smaller when the As antisite is positively charged (about 40 meV/GPa).

(4) The pressure dependence of the formation energies of the As antisite in GaAs is similar to the results obtained in Ref. 2 (75 meV/GPa and 35 meV/GPa for the neutral and the charged states, respectively) while we have obtained a much stronger pressure dependence for the formation energy of the Ga vacancy (our values of -70 meV/GPa up to -85 meV/GPa, depending on charge state, in comparison with -15 meV/GPa and -50 meV/GPa for neutral and -3 charge states, respectively, as obtained by Bonapasta and Giannozzi²). It follows from the present calculations that contrary to the conclusion in Ref. 2 it is feasible to control the formation of vacancies in GaAs because quite small formation energies may be achieved for these defects under hydrostatic pressure (see Fig. 4).

IV. SUMMARY

We have studied the influence of hydrostatic pressure on the formation energies and energy levels of cation vacancies in AlN, GaN, and GaAs as well as the As antisite in GaAs. We have found much stronger dependence of the formation energies and level positions of these defects on pressure in the case of GaAs than in the nitrides, where these dependences are rather weak and seem to be of little practical use from the application point of view. However, one has to keep in mind that the bulk modulus of AlN and GaN (about 200 GPa) is almost three times the value for GaAs (72 GPa). It means that if we instead compare the volume dependence of the formation energy of the cation vacancy in GaAs and in

the nitrides, we still find that it is larger in GaAs, but the difference is less pronounced.

Contrary to the cation vacancies, the As antisite in GaAs exhibits positive dependence of the formation energy on pressure. Consequently, this defect may be favored by an external tensile strain, a situation that may occur in GaAs thin layers that are lattice matched to an InGaAs substrate. The present work confirms the conclusion of Ref. 2 that ap-

plication of strain may allow *defect engineering* in the case of GaAs, whereas such methods seem less feasible for the III-V nitrides.

ACKNOWLEDGMENTS

This work was supported by the Committee of Scientific Research (Poland) under Grant No. KBN 2P03B 047 19 and by the Danish Rectors Conference.

-
- ¹J. Neugebauer and C.G. Van de Walle, Phys. Rev. B **50**, 8067 (1994).
²A.A. Bonapasta and P. Giannozzi, Phys. Rev. Lett. **84**, 3923 (2000).
³N.E. Christensen and I. Gorczyca, Phys. Rev. B **50**, 4397 (1994).
⁴I. Gorczyca, A. Svane, and N.E. Christensen, Phys. Rev. B **60**, 8147 (1999).
⁵M. Methfessel, Phys. Rev. B **38**, 1537 (1988).
⁶O.K. Andersen, Phys. Rev. B **12**, 3060 (1975).
⁷D. Glötzel, B. Segal, and O.K. Andersen, Solid State Commun. **36**, 403 (1980).
⁸R.O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 681 (1989).
⁹J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
¹⁰D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
¹¹A. Amore Bonapasta, Phys. Rev. B **51**, 4172 (1995).
¹²A. Rubio, J.L. Corkill, M.L. Cohen, E.L. Shirley, and S.G. Louie, Phys. Rev. B **48**, 11 810 (1993).
¹³M. Schlüter and G. A. Baraff, in *Proceedings of the 18th International Conference on Physics of Semiconductors*, edited by O. Engström (World Scientific, Singapore, 1987), Vol. 2, p. 793.
¹⁴Y. Bar-Yam and J.D. Joannopoulos, Phys. Rev. Lett. **56**, 1213 (1986).
¹⁵C. Delerue, Phys. Rev. B **44**, 10 525 (1991).
¹⁶M.J. Caldas, J. Dabrowski, A. Fazzio, and M. Scheffler, Phys. Rev. Lett. **65**, 2046 (1990).
¹⁷B.K. Meyer, J.M. Spaeth, and M. Scheffler, Phys. Rev. Lett. **52**, 851 (1984).
¹⁸M.K. Nissen, A. Villemaire, and M.L.W. Thewalt, Phys. Rev. Lett. **67**, 112 (1991).
¹⁹A. Amore Bonapasta, Phys. Rev. B **58**, 10 378 (1998).