Electrical activity of hydrogen impurities in GaSb: First-principles calculations

A. Peles, A. Janotti, and C. G. Van de Walle
Materials Department, University of California, Santa Barbara, California 93106-5050, USA
(Received 4 February 2008; revised manuscript received 2 June 2008; published 10 July 2008)

Gallium antimonide exhibits a high unintentional *p*-type conductivity, which is conventionally attributed to native point defects. Our first-principles calculations, based on density-functional theory with inclusion of spin-orbit interactions, provide evidence that isolated hydrogen in GaSb acts as a source of *p*-type doping; it can be incorporated in high concentrations and acts as a shallow acceptor. We also report results for diffusion barriers, for frequencies of local vibrational modes, and for interstitial H_2 molecules.

DOI: 10.1103/PhysRevB.78.035204 PACS number(s): 61.72.J−, 61.72.jj, 66.30.J−, 71.55.Eq

I. INTRODUCTION

GaSb is an interesting material from both a fundamental and an applied perspective.[1] Its optical and electronic properties allow applications in the areas of high-speed electronic devices, infrared (IR) optics, and renewable energy.[1] Its high electron mobility together with a unique combination of band gaps and band offsets with several lattice matched compound semiconductors makes GaSb suitable for high electron mobility transistors. Its relatively low band gap (0.82 eV at 0 K) (Ref. 1) makes it useful for IR detectors and sources. GaSb-based structures can also be used as booster cells in tandem solar cell arrangements and high efficiency thermophotovoltaic (TPV) cells.[2,3]

When not intentionally doped, GaSb invariably exhibits unintentional *p*-type conductivity with a typical carrier concentration of $\sim 10^{17}$ cm^{-3} regardless of growth technique and conditions. Native point defects have traditionally been invoked to explain this conductivity.[4,5] Understanding the underlying causes of this conductivity, and controlling the concentration of electrically active impurities and defects is key to the development of advanced devices based on this material.

Hydrogen is known to have important effects on the electronic properties of many semiconductors. The phenomenon of hydrogen passivation—the ability of hydrogen to diffuse through the lattice and complex with dangling bonds associated with point defects, thus, neutralizing their electrical activity—is well known and technologically important. Hydrogen can also passivate electrically active dopants.[6] Hydrogen typically behaves as an amphoteric impurity: in *p*-type material, it appears in a positive charge state (H^+), and thus, neutralizes the electrical activity of acceptors while in *n*-type material, it appears as H^- and neutralizes the activity of donors. It has been found, however, that in certain semiconductors, such as ZnO (Ref. 7) and InN (Ref. 8), hydrogen behaves exclusively as a donor and therefore acts as a source of conductivity.

Hydrogen can easily be incorporated in materials. Furthermore, hydrogen is intentionally or unintentionally present in most semiconductor growth environments, as well as during post-growth processing. Understanding the electrical activity of hydrogen in the material is therefore important. Several experimental studies of hydrogen interactions with GaSb have been published[9–11] but they have reported inconsistent results. All studies find that the passivation of donor and acceptors is asymmetric but Polyakov *et al.*[9] and Dutta *et al.*[10] report that hydrogen is more effective in passivating acceptors. Sestakova *et al.*[11] report that donors are more readily passivated. Our current work addresses the behavior of hydrogen based on first-principles calculations and aims to resolve these controversies.

In this paper we used first-principles calculations to study the incorporation of hydrogen in GaSb in *atomic* as well as *molecular* form. For monatomic interstitial hydrogen we report on the formation energies and local lattice relaxations, the diffusion barrier, and the local vibrational frequencies. Our results show that interstitial hydrogen in GaSb is not amphoteric but acts exclusively as an acceptor. Hydrogen can therefore be a source of *p*-type conductivity in GaSb and may contribute to the observed unintentional conductivity.

II. METHODS

We perform first-principles calculation based on density-functional theory (DFT) (Refs. 12 and 13) and the projector augmented wave (PAW) method.[14] We consider relativistic effects by including scalar-relativistic effects (through the pseudopotentials) and also spin-orbit interactions. PAW potentials with valence states $4s^2 3p^1$ for Ga, $5s^2 5p^3$ for Sb, and $1s^1$ for H were used, as implemented in the Vienna *ab initio* simulation package (VASP).[15] The electron exchange-correlation energy was evaluated using the local-density approximation (LDA). Impurity calculations were performed in a supercell geometry with 64 atoms in the supercell. The Brillouin zone was sampled using the Monkhorst-Pack technique;[16] a shifted $2 \times 2 \times 2$ grid was found sufficient for a 64-atom supercell. The cut-off energy for plane-wave expansions was 200 eV.

III. RESULTS AND DISCUSSION

A. Bulk GaSb

The crystal structure of GaSb is zinc blende with the $F\bar{4}3m$ space group. The calculated lattice parameter a $=6.06$ Å is 0.5% smaller than the experimental value of 6.0959 Å.[17] The total energies for bulk Ga and Sb were calculated in their respective crystal symmetries, Cmca and $R\bar{3}m$. The calculated enthalpy of formation of GaSb is

 ©2008 The American Physical Society

TABLE I. Band energies in eV at the Γ point relative to the valence-band maximum. The bands calculated with SO splitting are labeled in double group notation.

Symmetry at Γ	Degeneracy	Eigenvalue	Experiment
Without SO			
Γ_{1v}	2	−11.69	
Γ_{15v}	6	0	
Γ_{1c}	2	0.12	
Γ_{15c}	6	2.16	
With SO			
Γ_{6v}	2	−11.92	−11.64 [a]
Γ_{7v}	2	−0.73	−0.82 [a],−0.76[b]
Γ_{8v}	4	0	
Γ_{6c}	2	−0.11	0.82[b]
Γ_{7c}	2	2.38	3.19[b]
Γ_{8c}	4	2.59	3.40[b]

[a]Reference 21.
[b]Reference 22.

−0.48 eV, which agrees well with the experimental value of −0.43 eV.[18] The measured low-temperature band gap of GaSb is E_g=0.8 eV.[1] Our calculated value (without spin-orbit splitting) for E_g is 0.12 eV, exhibiting the well-known shortcoming of DFT-LDA, related to the self-interaction error and the absence of a discontinuity in the exchange-correlation functional derivative with respect to electron occupation number. However, it is expected that LDA adequately represents exchange and correlation in the valence-band states, and although Kohn-Sham eigenvalues do not have a strict physical meaning (except for the highest occupied level[19]), they often compare reasonably well with experiment.

GaSb exhibits substantial relativistic effects, evidenced by large spin-orbit (SO) splittings.[1] Here we focus our attention on the SO splitting of the topmost valence band at the center of the Brillouin zone as the position of the valence-band maximum (VBM) is relevant for the determination of the formation energy of charged impurities. In the nonrelativistic limit, the highest valence band at the Γ point (Γ_{15}) is sixfold degenerate (including the spin degeneracy) and dominated by p-like atomic orbitals. Spin-orbit interactions split this degeneracy into fourfold-degenerate (Γ_8) and twofold-degenerate (Γ_7) states. The Γ_8 states are shifted up by $\frac{1}{3}\Delta_0$ and the Γ_7 states are shifted down by $\frac{2}{3}\Delta_0$ with respect to Γ_{15}.[20] The calculated eigenenergies at the Γ point with and without inclusion of spin-orbit interaction are compared with experiment in Table I. The experimental value of the spin-orbit splitting energy in GaSb is Δ_0=0.80 eV, which is of the order of the band gap.[1] Our calculated value of 0.73 eV is in reasonable agreement with experiment. We find an upward shift in the VBM by $\frac{1}{3}\Delta_0$=0.24 eV. This shift reduces the band gap at the Γ point, leading to a negative band gap in our fully relativistic calculation. Because of the large magnitude of the spin-orbit splitting, it is clearly important to take these relativistic effects into account when studying electronic levels in GaSb.

Table I shows that the calculated valence-band energies agree reasonably well with experiment except for a slight overestimate of the bandwidth (by ∼0.3 eV). The conduction bands, on the other hand, are too low in energy by ∼0.8–0.9 eV. At the Γ point, the lowest conduction band (Γ_6) crosses below the valence band. This negative gap actually does not create any problems for our total-energy calculations. Indeed, the incorrect ordering of valence and conduction bands occurs only over a very small portion of the Brillouin zone in the immediate vicinity of the Γ point. As mentioned above, our integrations over the Brillouin zone are performed using a set of **k** points determined by a shifted 2×2×2 grid in the Monkhorst-Pack scheme.[16] This grid does not contain any points in the vicinity of the Γ point where the gap would be negative. At each of the **k** points that are included in the grid, the bands are correctly occupied and hence produce the correct contribution to the total energy. The negative gap that occurs over a small portion of the Brillouin zone therefore has no consequences for the calculated total energies.

B. Interstitial monatomic hydrogen

The first-principles approach allows us to calculate the local structure and formation energy of a hydrogen impurity in the lattice. The formation energy is expressed as[23]

$$E^f(\mathrm{H}^q) = E_{tot}(\mathrm{H}^q) - E_{tot}(\mathrm{bulk}) - \mu_\mathrm{H} + qE_F. \quad (1)$$

The first two terms are the total energy of the supercell containing a hydrogen interstitial in charge state q and the total energy of bulk GaSb in the supercell geometry, respectively. E_F is the energy of electrons that are exchanged between a defect and the reservoir of electrons, i.e., the electron chemical potential or Fermi level. Below we will reference E_F to the VBM of bulk GaSb. The shift in the reference level for electrostatic potentials between the bulk and the defect supercell was taken into account by properly aligning the two.[23] The reference for the hydrogen chemical potential μ_H is the ground-state energy of an H_2 molecule at 0 K.

First, we address an isolated hydrogen interstitial in GaSb in three possible charge states q (+1, 0, −1). For each charge state, different possible interstitial sites were explored in order to locate the equilibrium position. These include sites of T_d, C_{3v}, C_{2v}, and C_s symmetry, as well as other sites where the hydrogen atom was randomly displaced from a high-symmetry site and no symmetry was assumed. In tetrahedral symmetry we consider interstitial sites surrounded by four Ga atoms, T_{Ga}, or by four Sb atoms, T_{Sb}. In C_{3v} symmetry we consider sites that are commonly referred to as the bond center (BC), antibonding sites located on the extension of a GaSb bond near either a Ga (AB_{Ga}) or an Sb atom (AB_{Sb}), and the hexagonal site (Hex). Sites of C_{2v} symmetry include the C_{Ga} and C_{Sb} sites, which occur midway between two adjacent Ga or Sb atoms. The symmetry sites are illustrated in Fig. 1.

Table II lists formation energies [Eq. (1)] for various low energy stable and metastable sites, with (E^f_{SO}) and without (E^f) inclusion of spin-orbit interactions. The stable configuration (global minimum) for neutral (H_i^0) and positively

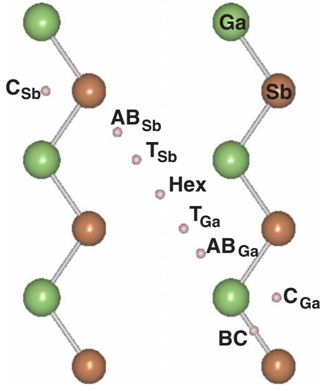

FIG. 1. (Color online) Schematic of high-symmetry sites for interstitial hydrogen in the $(1\bar{1}0)$ plane.

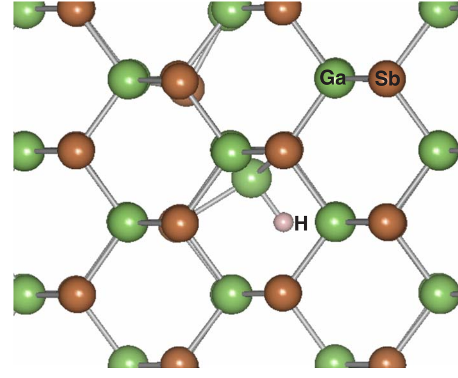

FIG. 2. (Color online) Local atomic relaxations around a hydrogen interstitial at an AB_{Ga} site in the negative charge state. Note the large displacements of the Ga atom and its Sb neighbor.

charged (H_i^+) interstitials is found at the bond-center site. Similar local lattice relaxations are observed for H_i^0 and H_i^+. For H_i^0, the hydrogen impurity at the bond center pushes the surrounding Ga and Sb atoms outward along the bond, and away from their equilibrium positions, resulting in a Ga-H distance of 1.75 Å and an Sb-H distance of 1.82 Å. The Ga and Sb atoms are displaced by 0.45 and 0.49 Å from their equilibrium positions, respectively. In the case of H_i^+, interstitial hydrogen is equidistant (1.78 Å) from the adjacent Ga and Sb atoms, which are displaced by 0.50 and 0.44 Å from their equilibrium positions. Negatively charged hydrogen interstitials, H_i^-, favor an antibonding site near a Ga atom (AB_{Ga}) and cause significant local lattice relaxations, as shown in Fig. 2. The H atom bonds with the Ga atom, resulting in a breaking of the bond between that Ga atom and its Sb neighbor along the Ga-H bond axis. The Ga atom that bonds to the H atom is displaced from its bulk equilibrium position by 1.01 Å toward the T_{Ga} site while the Sb atom adjacent to this Ga atom moves by 0.32 Å in the direction of the Ga atom. The Ga-H bond length is 1.66 Å.

The comparison of calculations with and without spin-orbit interactions indicates that there are significant differences in the formation energies. However, these differences are almost completely attributable to the different position of the VBM in the calculations that include spin-orbit interactions. This upward shift of the VBM (by our calculated value of $\frac{1}{3}\Delta_0=0.24$ eV) leads to an increase in the formation energy of positively charged defects and a decrease in E^f of negatively charged defects.

TABLE II. Calculated formation energies E^f [as defined in Eq. (1)] for an interstitial hydrogen impurity in all three possible charge states at various stable and metastable sites in GaSb. The Fermi level E_F is assumed to be at the valence-band maximum.

Charge state	Site	E^f	E^f_{SO} (eV)
H^-	AB_{Ga}	1.14	0.90
H^-	AB_{Sb}	1.42	1.18
H^-	C_{Sb}	1.23	0.98
H^+	BC	0.90	1.14
H^+	C_{Sb}	1.28	1.52
H^+	AB_{Sb}	1.40	1.64
H^0	BC	1.33	1.33
H^0	T_{Sb}	1.69	1.69

Figure 3 shows formation energies of the hydrogen interstitial as a function of Fermi energy. The Fermi energy is referenced to the VBM (which includes spin-orbit interactions). It is clear from Fig. 3 that H_i^- is the most stable state for any position of the Fermi level in the band gap (and down to 0.12 eV below the VBM). As a consequence, interstitial hydrogen in GaSb behaves exclusively as an acceptor, accommodating two electrons in the defect level, and contributing a hole as a free charge carrier. Combined with the modest formation energies, which indicate a high solubility, these results indicate that interstitial hydrogen can be a source of unintentional doping in GaSb. Our results indicate that if we try to bind a hole (or two holes) to the hydrogen center (i.e., if we try to make hydrogen neutral or positively charged), these holes will not be localized near the hydrogen since their energy level is resonant with the valence band; instead, the hole would be bound to the negatively charged hydrogen center in a "hydrogenic effective-mass state." The ionization energy of the hydrogen acceptor will thus be determined by effective-mass theory, and can be estimated based on the hole effective mass and the dielectric constant of the host material, just like for other shallow acceptors.

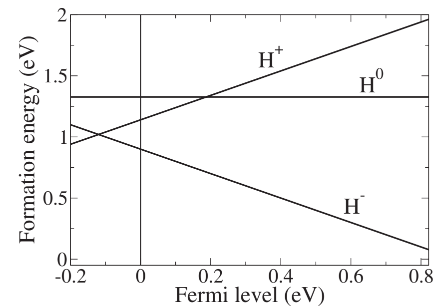

FIG. 3. Calculated formation energies of hydrogen interstitials in GaSb as a function of Fermi level. For each charge state the energy of the most stable configuration is shown (see Table II). Spin-orbit interactions are included and the valence-band maximum (including spin-orbit splitting) is set to 0.

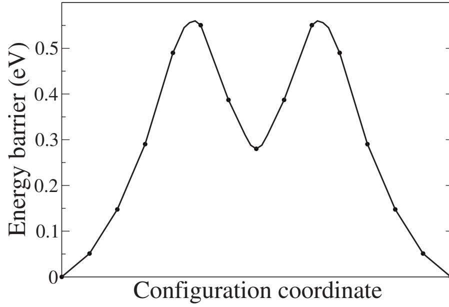

FIG. 4. Calculated energies of H_i^- along the minimum-energy migration path. The path starts and ends at the global minimum (AB_{Ga}). A local minimum is at AB_{Sb}. The highest energy represents the barrier height and corresponds to the hexagonal interstitial site.

Using published values,[1] this leads to an ionization energy of 0.02 eV.

Vibrational spectroscopy is an important tool for establishing the presence of hydrogen in the lattice as well as for identifying its microscopic structure. We have therefore investigated local vibrational modes related to H_i^- at AB_{Ga}. The vibrational frequencies are calculated here within the harmonic approximation. The Ga-H stretching and wagging mode frequencies are 1518 and 610 cm^{-1}, respectively. The stretching mode is well above the GaSb phonon spectrum and should easily be identified in experiments. Anharmonic corrections were not included here; they tend to shift the frequency of the stretching mode down by an amount that could be on the order of 50 cm^{-1}.[24] The values reported here may be useful in the interpretation of future measurements.

We also address the mobility of the hydrogen interstitial by calculating the minimum-energy diffusion path for H_i^-, as shown in Fig. 4. The calculations of the diffusion path and barrier were performed using the nudged elastic band method.[25] Hydrogen diffusion between two global minima at AB_{Ga} is symmetric with respect to T_{Sb}, which is a local minimum. The calculated energy barrier for hydrogen diffusion is 0.57 eV; the saddle point corresponds to the hexagonal interstitial site. Experimental measurements of diffusion coefficients for hydrogen in GaSb suggested barrier heights of 0.45 eV in *p*-type material and 0.55 eV in *n*-type material.[9]

Our results in this section pertain to isolated interstitial hydrogen with the key conclusion that only the negative charge state is stable. We have not explicitly performed calculations for hydrogen interacting with other dopant impurities or with native defects. Nevertheless, based on experience relating to hydrogen in other semiconductors,[26] we can make some qualitative comments about the pattern of interactions between hydrogen and other dopants. Figure 3 shows that the formation energy of interstitial hydrogen depends on the Fermi level. Let us assume that the concentration of interstitial hydrogen is much lower than that of other electrically active impurities or defects; the Fermi level in the material is then determined by those other impurities or defects. Figure 3 tells us that for *any* Fermi-level position, interstitial hydrogen occurs as H^-, i.e., it is always negatively charged. This conclusion immediately provides insight into the qualitative interaction between hydrogen and dopants: since H^- is electrostatically repelled by negatively charged centers, it will not approach dopants or defects that act as acceptors. Interstitial hydrogen in GaSb is therefore not able to compensate or passivate acceptor dopants. This is in contrast to the behavior of hydrogen in the majority of other semiconductors, such as Si, GaAs, or GaN (Refs. 26 and 27): in those materials, hydrogen behaves as an amphoteric impurity and would be stable in a positive charge state (H^+) in *p*-type material. In this charge state, hydrogen is able to neutralize the electrical activity of acceptors. Since H^+ is never stable in GaSb, neutralization of acceptors cannot occur.

TABLE III. Calculated formation energies E^f for an interstitial hydrogen molecule with its center of mass situated at various high-symmetry sites in the lattice, as well as in different orientations.

Site	Orientation	E^f (eV)	d_{H-H} (Å)
T_{Ga}	⟨100⟩	0.209	0.785
T_{Ga}	⟨111⟩	0.218	0.787
T_{Sb}	⟨111⟩	0.409	0.786
T_{Sb}	⟨100⟩	0.403	0.784

One could speculate that *complexes* between hydrogen and other defects or impurities could be formed already during the growth of the material; however, such complexes rarely have sufficient binding energy to be stable during growth or processing.[23] Our findings about isolated interstitial hydrogen are therefore likely to be relevant to the overall behavior and stability of hydrogen-related species in GaSb.

Comparisons with experiment[9–11] may be complicated by the fact that during hydrogenation experiments, hydrogen may interact not only with the dopant impurities that were intentionally introduced but also with other electrically active centers (impurities or native defects) that are unintentionally present. In addition, it is possible that hydrogen induces the formation of new defects. Such phenomena would complicate the interpretation of experimental results.

C. Interstitial hydrogen molecules

We have also studied incorporation of molecular hydrogen in the GaSb lattice. Table III lists the formation energies and H-H bond lengths for H_2 molecules at tetrahedral interstitial sites in the GaSb lattice in two different orientations (⟨111⟩ and ⟨100⟩). The lowest energy position for the H_2 molecule is at the T_{Ga} site. Different orientations lead to very similar energies, the ⟨111⟩ direction leading to an energy only 0.009 eV higher than the ⟨100⟩ direction. This suggests a very small barrier for reorientation and rotation at the T_{Ga} site. The formation energy at the T_{Sb} site is ~0.2 eV higher than at T_{Ga}, consistent with the trend observed in other compound semiconductors:[28] H_2 at the tetrahedral site surrounded by cations systematically has a lower energy than at the tetrahedral site surrounded by anions. The presence of the H_2 molecule does not induce any significant local lattice relaxations. As shown in Table III, the molecular distance of the H_2 molecule incorporated in the GaSb lattice is slightly longer than the calculated bond length in vacuum (0.767 Å). The vibrational frequency of the H_2 molecule at the T_{Ga} site, calculated within the harmonic approximation, is

3610 cm^{-1}. In spite of the low formation energy of H_2, the concentration of interstitial H_2 is expected to be rather small. Indeed, hydrogen is usually incorporated into semiconductors in atomic form, and since monatomic H in GaSb occurs exclusively in the negative charge state, subsequent formation of H_2 will be inhibited due to Coulomb repulsion between the monatomic species.

IV. SUMMARY AND CONCLUSIONS

We have presented a first-principles study of the properties of monatomic and molecular hydrogen in the GaSb semiconductor. Unlike the amphoteric behavior of hydrogen in other III–V semiconductors, monatomic hydrogen interstitials in GaSb occur exclusively in the negative charge state. Hydrogen therefore acts as a shallow acceptor, suggesting that interstitial hydrogen can act as a source of *p*-type conductivity in GaSb. Significant lattice relaxations are present when H_i^- is incorporated in the GaSb lattice with formation of a Ga-H bond and breaking of a Ga-Sb bond. The large spin-orbit interactions in GaSb and consequent splitting of the VBM have to be taken into account when determining the electrical behavior of interstitial hydrogen. The energy barrier for the H_i^- diffusion is 0.57 eV. Hydrogen molecules located at the T_{Ga} are also quite stable in GaSb but their formation will be suppressed due to Coulomb repulsion between the monatomic species, which are always negatively charged. Our study suggests that hydrogen can be used to passivate donors in GaSb but not to control the unintentional *p*-type conductivity; indeed, hydrogen is found here to contribute to that unintentional conductivity.

ACKNOWLEDGMENTS

A.P. acknowledges financial support by the Natural Sciences and Engineering Research Council of Canada (NSERC). This work was supported in part by the Semiconductor Research Corporation Nonclassical CMOS Research Center (Contract No. 2006-VC-1437). It made use of MRL Central Facilities supported by the NSF MRSEC Program under Grant No. DMR05-20415, and of the CNSI Computing Facility under NSF Grant No. CHE-0321368.

[1] P. S. Dutta, H. L. Bhat, and V. Kumar, J. Appl. Phys. **81**, 5821 (1997).
[2] L. M. Frass, G. R. Girard, J. E. Avery, B. A. Arau, V. S. Sundaram, A. G. Thompson, and J. M. Gee, J. Appl. Phys. **66**, 15 (1989).
[3] A. W. Bett and O. V. Sulima, Semicond. Sci. Technol. **18**, S184 (2003).
[4] R. D. Baxter, F. J. Reid, and A. C. Beer, Phys. Rev. **162**, 718 (1967).
[5] M. Hakala, M. J. Puska, and R. M. Nieminen, J. Appl. Phys. **91**, 4988 (2002).
[6] J. I. Pankove, D. E. Carlson, J. E. Berkeyheiser, and R. O. Wance, Phys. Rev. Lett. **51**, 2224 (1983).
[7] C. G. Van de Walle, Phys. Rev. Lett. **85**, 1012 (2000).
[8] E. A. Davis, S. F. J. Cox, R. L. Lichti, and C. G. Van de Walle, Appl. Phys. Lett. **82**, 592 (2003).
[9] A. Y. Polyakov, S. J. Pearton, R. G. Wilson, R. Eai-Choudhury, R. J. Hillard, X. J. Bao, M. Stam, A. J. Milnes, T. E. Schlesinger, and J. Lopata, Appl. Phys. Lett. **60**, 1318 (1992).
[10] P. S. Dutta, K. S. Sangunni, H. L. Bhat, and V. Kumar, Phys. Rev. B **51**, 2153 (1995).
[11] V. Sestakova, B. Stepanek, J. J. Mares, and J. Sestak, J. Cryst. Growth **140**, 426 (1994).
[12] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
[13] W. Kohn and L. Sham, Phys. Rev. **140**, A1133 (1965).
[14] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
[15] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[16] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[17] M. E. Straumanis and C. D. Kim, J. Appl. Phys. **36**, 3822 (1965).
[18] *Handbook of Chemistry and Physics*, 76th ed. (CRC, Boca Raton, 1995).
[19] J. F. Janak, Phys. Rev. B **18**, 7165 (1978).
[20] P. Y. Yu and M. Cardona, *Fundamentals of Semiconductors: Physics and Materials Properties* (Springer, Berlin, 2001).
[21] T. C. Chiang and D. E. Eastman, Phys. Rev. B **22**, 2940 (1980).
[22] D. E. Aspnes, C. G. Olson, and D. W. Lynch, Phys. Rev. B **14**, 4450 (1976).
[23] C. G. Van de Walle and J. Neugebauer, J. Appl. Phys. **95**, 3851 (2004).
[24] A. Janotti, S. B. Zhang, and S.-H. Wei, Phys. Rev. Lett. **88**, 125506 (2002).
[25] G. Henkelman and H. Jonsson, J. Chem. Phys. **113**, 9978 (2000).
[26] C. G. Van de Walle and J. Neugebauer, Annu. Rev. Mater. Res. **36**, 179 (2006).
[27] C. G. Van de Walle and J. Neugebauer, Nature (London) **423**, 626 (2003).
[28] C. G. Van de Walle, Phys. Rev. Lett. **80**, 2177 (1998).