

Stacking fault effects in Mg-doped GaN

T. M. Schmidt and R. H. Miwa

Departamento de Ciências Físicas, Universidade Federal de Uberlândia, CP 593, CEP 38400-902, Uberlândia, MG, Brazil

W. Orellana

Instituto de Física, Universidade de São Paulo, CP 66318, CEP 05315-970, São Paulo, SP, Brazil

H. Chacham

Departamento de Física, ICEx, Universidade Federal de Minas Gerais, CP 702, CEP 30123-970, Belo Horizonte, MG, Brazil

(Received 8 August 2001; published 2 January 2002)

First-principles total energy calculations are performed to investigate the interaction of a stacking fault with a p -type impurity in both zinc-blende and wurtzite GaN. For both structures we find that, in the presence of a stacking fault, the impurity level is a more localized state in the band gap. In zinc-blende GaN, the minimum energy position of the substitutional Mg atom is at the plane of the stacking fault. In contrast, in wurtzite GaN the substitutional Mg atom at the plane of the stacking fault is a local minimum and the global minimum is the substitutional Mg far from the fault. This behavior can be understood as a packing effect which induces a distinct strain relief process, since the local structure of the stacking fault in zinc-blende GaN is similar to fault-free wurtzite GaN and vice-versa.

DOI: 10.1103/PhysRevB.65.033205

PACS number(s): 61.72.Nn, 61.72.Bb, 61.72.Ji, 71.55.Eq

I. INTRODUCTION

Efficient GaN-based optoelectronic devices operating in the blue/ultraviolet spectra regions remain the subject of much attention due to its great technological importance. GaN usually crystallizes in the wurtzite (hexagonal) structure and it has been successfully grown in the zinc-blende (cubic) structure.¹ Mg is widely used as dopant to obtain p -type GaN where light-emitting devices attaining high p -type conductivity are currently available. However, recent studies have shown that the incorporation of a high level of Mg during growth might be associated with the formation of extended defects.^{2,3}

Dopants in semiconductors in the presence of extended defects can alter the electronic and structural properties of the material, which under certain conditions can be even detrimental. It is known that the simple presence of stacking faults perturbs the levels at the valence band maximum (VBM) and at the conduction band minimum (CBM) in zinc-blende semiconductors as silicon and GaAs.^{4,5} In nitrides the concentration of extended defects is usually higher than in other III-V semiconductors, mainly due to the lattice mismatch at the substrates.⁶ Stacking faults in GaN have been attributed to be responsible for electronic confinement,^{7,8} and for inducing spontaneous ordering in p -type systems.² In the present work we perform first-principles investigations on the interaction of a stacking fault (SF) with a p -type dopant in zinc-blende (zb) and wurtzite (w) GaN. As it has been observed for other zb semiconductors,^{5,9} we find that in zb-GaN the SF works as an attractive potential for the Mg atom. In contrast, in w-GaN the Mg atom prefers to stay far from the fault plane. The impurity level always becomes more localized in the presence of the SF. The unexpected behavior of the Mg-doped w-GaN in the presence of an extended defect can be understood as a packing-structural effect.

II. METHOD OF CALCULATION

Our calculations were performed in the framework of the density-functional theory¹⁰ within the local-density approximation¹¹ using the SIESTA program.¹² Ga, N, and Mg atoms are described by norm-conserving *ab initio* pseudopotentials generated by the scheme of Troullier and Martins¹³ in the Kleinman-Bylander separable form.¹⁴ Core-valence interaction due to the Ga $3d$ electrons were included using the nonlinear core correction.¹⁵ The Kohn-Sham wave functions are expanded using an atomic orbital basis set, consisting of finite-range pseudoatomic wave functions of the type introduced by Sankey and Niklewski,¹⁶ with a common orbital-confinement energy of 0.1 eV. A double- ζ basis set is used to represent the valence wave functions in the reciprocal space with an equivalent plane-wave mesh cutoff of 80 Ry. We use a 160-atom supercell to simulate the zinc-blende structure, where a double atomic layer along the $[111]$ direction is removed in order to form the so-called intrinsic SF. To simulate the SF in the wurtzite structure we use a 192-atom supercell. Due to the large size of the supercells considered here, only the Γ point was used to sample the Brillouin zone in all the calculations. We test the K space summation by using four special k points to sample the Brillouin zone (BZ) for Mg in zinc-blende GaN, and our results give a total energy difference, as compared to the results using the Γ point, less than 1 meV/cell. The positions of all the atoms in the supercells were relaxed until all force component were smaller than 0.05 eV/Å.

The determination of the theoretical equilibrium geometry of zb- and w-GaN was performed by variable-cell calculations allowing lattice vectors and atomic positions of the unit cells to relax. For those calculations we consider a larger k -point sampling.¹⁷ Our results for the equilibrium lattice constants are $a = 4.51$ Å for zb-GaN and $a = 3.23$ Å and $c = 5.19$ Å for w-GaN, in good agreement with available ex-

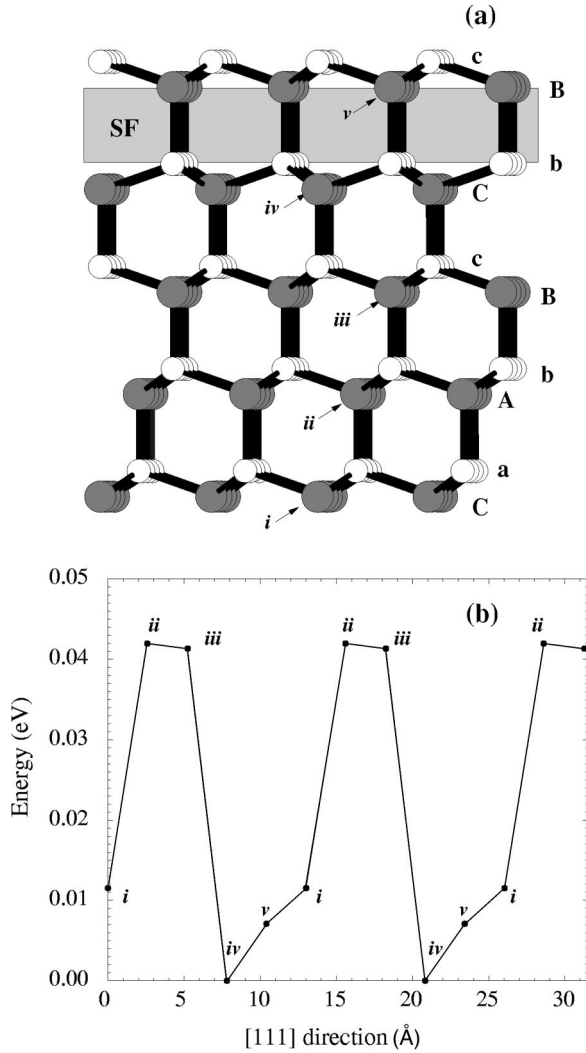


FIG. 1. (a) Atomic arrangement of the supercell in the zinc-blende structure, where a SF has been created (shadow lane); and (b) total energy as a function of the Mg position as indicated in (a).

perimental data,¹⁸ within an accuracy of 1%. The band structure calculations of zb-GaN and w-GaN show a direct energy band gap of 2.01 and 2.37 eV, respectively, in close agreement with other theoretical calculations.¹⁸

III. RESULTS

A. Mg in zinc-blende GaN

An intrinsic fault in the stacking sequence of the zinc-blende GaN has been simulated in order to understand the interaction of the fault with an acceptor impurity. The normal sequence in the [111] close-packed direction for zinc-blende semiconductors is ... AaBbC-cAaBbCc ..., each letter representing a stacking plane. In our simulated intrinsic SF we remove a double layer (Aa, for example) and glue together the remaining pieces of material. In Fig. 1(a) we show the supercell used to simulate this SF. Using the same cell and the same basis we calculate the total energy for a Mg atom occupying five different Ga sites along the [111] direction. These sites are labeled as *i*, *ii*, *iii*, *iv*, and *v* in Fig. 1.

According to our results, the energetically most stable position for the Mg atom is at the fault plane (*iv*), whereas far from the fault plane (*ii*), the Mg position is energetically the least favorable [see Fig. 1(b)]. The stable position for the Mg at the fault plane seems to be a general tendency for dopants in zinc-blende semiconductors. An energy reduction has been verified in *n*-type and *p*-type silicon⁹ and in Si-doped GaAs,⁵ when the impurity is on the fault plane.

Substitutional Mg at a Ga site in perfect zb-GaN (without SF) has been calculated using a 128-atom supercell. Our results show that the Mg impurity perturbs the top of the valence band inducing a small splitting of the one-electron energy levels (a_1+e). We have also observed a nearly symmetrical outward relaxation of the neighboring nitrogen by 2.3% with respect to the unrelaxed positions, due to the presence of the Mg impurity.

In the presence of a SF, the Mg-induced properties shows a different picture. The simple presence of a SF (without Mg) breaks the translational symmetry of the crystal, splitting the threefold-degenerated state at the VBM into a_1+e states, where the e state lies above the a_1 state by ~ 30 meV. The Mg atom at the Ga site induces an energy split of the e state. In addition, we observe that the highest occupied energy level enters in the band gap by around 15 meV when the Mg atom is at the fault plane compared to the Mg far from the fault.

The atomic relaxations around the impurity are similar for Mg far from and close to the fault plane. However, they differ from the fault-free structure, which now are more asymmetric. The first-neighbor N atoms relax outward by about 2.2%, where the Mg-N bond along the [111] direction is slightly larger than the other three Mg-N bonds.

B. Mg in wurtzite GaN

Similarly as the zb structure, we study the effect of the extended defect in w-GaN:Mg by placing the impurity in six different positions as indicated in Fig. 2. Among the different ways to obtain a SF in w-GaN, we have considered the SF structure schematically shown in Fig. 2(a), which exhibits one of the lowest formation energy.⁸ Differently as found for zb-GaN:Mg, the lowest energy configuration for the Mg impurity in w-GaN along the hexagonal c axis, occurs with Mg occupying a Ga site far from the fault plane [see Fig. 2(b)]. This result indicates that the observed spontaneous ordering of w-GaN:Mg with Mg forming planar defects² is a result of kinetic effects during the growth process rather than due to energetic stability.

The Mg impurity in perfect w-GaN (without SF) has been calculated using a 192-atom supercell. Our results for the structural and electronic properties are quite different from those found for Mg in perfect zb-GaN. The equilibrium geometry shows an asymmetric outward relaxation around 2% with respect to the unrelaxed positions. The three basal Mg-N bonds are $\sim 4\%$ smaller than the Mg-N bond oriented along the c axis. The electronic charge density plot of the higher occupied energy levels of pure w-GaN (a_1+e) shows that the top of the valence band has a nitrogen p -like character [see Fig. 3(a)]. The charge density plot of the a_1 level

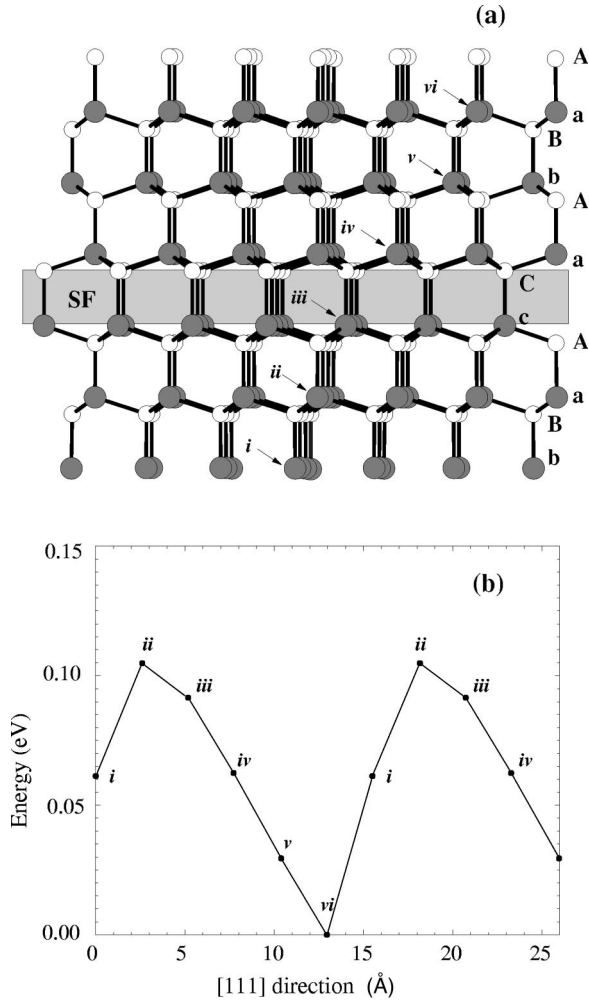


FIG. 2. (a) Atomic arrangement of the supercell in the wurtzite structure, where a SF has been created (shadow lane); and (b) total energy as a function of the Mg position as indicated in (a).

is shown in Fig. 3(b), similarly as observed for pure w-GaN, the electronic charge density is concentrated at the N atoms, preserving the orbital character of the VBM. In addition, we observe a strong charge localization at the first-neighbor N atoms, suggesting a noneffective mass level.¹⁹

The presence of a SF in w-GaN does not perturb the VBM as observed in the zb structure [see Fig. 3(c)]. However, we observe a larger charge localization of the highest occupied energy level when it is compared with the fault-free w-GaN [compare Figs. 3(a) and 3(c)]. We observe that the perturbation on the wave function is a long range effect, since it occurs not only on the fault plane, but also away from it. The apparent delocalization of the perturbation, in our calculation, can be attributed to the interaction between the cells (images). In the limit of very large supercells, we should expect that the perturbation on the wave function would decrease when moving further away from the stacking fault. Including the Mg impurity in the presence of a SF, we observe that the charge density of the a_1 level is very similar for Mg close to and far from the SF plane [compare Figs. 3(d) and 3(e)]. Nevertheless, in contrast of what occurs in the zb structure, the splitting of the higher occupied energy lev-

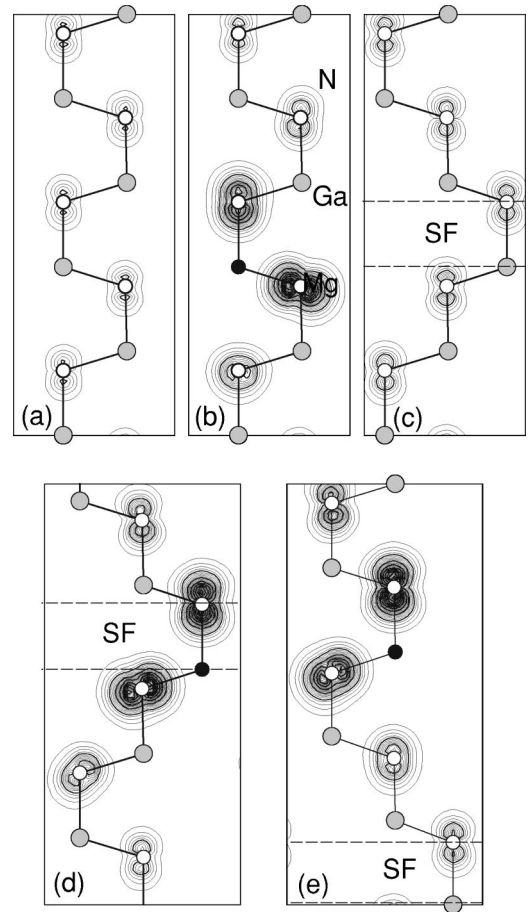


FIG. 3. Electronic charge density of the highest occupied level of the w-GaN: (a) for the pure material; (b) for the Mg impurity substitutional at the Ga site; (c) in the presence of a SF without impurity; (d) with a Mg atom positioned at the fault plane; and (e) with the Mg atom far from the fault plane. All plots are normalized to the same contour line intervals.

els increases by the proximity of the Mg impurity to the fault plane. Regarding the equilibrium geometry, the outward relaxation around the impurity for the w-GaN are larger in the presence of the SF, as in the case of zb-GaN. The basal Mg-N bonds relax by about 2%, while the Mg-N bond along the c axis relaxes more than 3%.

IV. DISCUSSION

The changes on the electronic structure of doped (n - and p -type) semiconductors due to the presence of SF are quite similar: The impurity level becomes deeper and more localized. For GaN (zinc blende and wurtzite) this is not different. However, the energetic of the Mg impurity in zb-GaN and w-GaN in the presence of the fault exhibits an opposite behavior. For w-GaN, the fault plane position for the impurity is not the most stable one. We can understand this behavior as a packing structure effect. The SF in zb-GaN is locally similar to fault-free w-GaN. The c/a ratio is 1.606 in w-GaN, which is smaller than the ideal one (1.633). Consequently, it allows higher strain relief around the impurity when it is close to the fault, lowering the total energy. On the

other hand, the SF in w-GaN is locally similar to the fault-free zb-GaN, where the packing structure is homogeneously higher, leading to an energetically less favorable situation due to the impurity induced relaxations. Another result which can reinforce this analysis is a direct calculation of the total energy difference between the Mg-doped w-GaN and zb-GaN, as compared to the pure material. Using the same supercell for each structure, our results show that w-GaN:Mg is energetically more stable than zb-GaN:Mg by about 0.2 eV per impurity. Although this value cannot be taken as the upper limit of the energy difference between the Mg position close to and far from the fault [because the SF changes the structure from zb (w) to w (zb) only locally], becomes clear that the Mg impurity prefers the wurtzite structure.

In summary, we show that for zb-GaN, the Mg impurity segregates towards the SF. However, for w-GaN the most

stable position for Mg is far from the SF plane. In both structures, the presence of the SF induces a localization of the Mg impurity level. The energetic difference between zb-GaN and w-GaN can be understood as a local packing effect, since the SF in zb-GaN (w-GaN) is locally similar to the fault-free w-GaN (zb-GaN). Although the electronic properties are very similar for the Mg impurity in zb-GaN and w-GaN in the presence of a fault, their energetics are quite different, suggesting that this behavior can be attributed to a local strain relief process.

ACKNOWLEDGMENTS

This work was supported by the Brazilian agencies FAPEMIG and CNPq. We also would like to thank the CENAPAD-MG/CO for computer time.

-
- ¹D.J. As, D. Schikora, A. Greiner, M. Lübbbers, J. Mimkes, and K. Lischka, *Phys. Rev. B* **54**, R11 118 (1996).
- ²Z. Liliental-Weber, M. Benamara, J. Washburn, I. Grzegory, and S. Porowski, *Phys. Rev. Lett.* **83**, 2370 (1999).
- ³L.T. Romano, J.E. Northrup, A.J. Ptak, and T.H. Myers, *Appl. Phys. Lett.* **77**, 2479 (2000).
- ⁴M.Y. Chou, M.L. Cohen, and S.G. Louie, *Phys. Rev. B* **32**, 7979 (1985).
- ⁵T.M. Schmidt, J.F. Justo, and A. Fazzio, *Appl. Phys. Lett.* **78**, 907 (2001).
- ⁶L.T. Romano, B.S. Krusor, and R.J. Molnar, *Appl. Phys. Lett.* **71**, 2283 (1997).
- ⁷M. Albrecht, S. Christiansen, G. Salvati, C. Zanotti-Fregonara, Y.T. Rebane, Y.G. Shreter, M. Mayer, A. Pelzmann, M. Kamp, K.J. Ebeling, M.D. Bremser, R.F. Davis, and H.P. Strunk, in *Gallium Nitride and Related Materials II*, edited by C.R. Abernathy, H. Amano, and J.C. Zolper, *Mater. Res. Soc. Symp. Proc.* **468** (Material Research Society, Pittsburgh, 1997), p. 293.
- ⁸C. Stampfl and Chris G. Van de Walle, *Phys. Rev. B* **57**, R15 052 (1998).
- ⁹A. Antonelli, J.F. Justo, and A. Fazzio, *Phys. Rev. B* **60**, 4711 (1999).
- ¹⁰P. Hohenberg, and W. Kohn, *Phys. Rev.* **136**, B864 (1964); W. Kohn and L.J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- ¹¹D.M. Ceperley, and B.J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980); J.P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- ¹²P. Ordejón, E. Artacho, and J.M. Soler, *Phys. Rev. B* **53**, 10 441 (1996); D. Sánchez-Portal, P. Ordejón, E. Artacho, and J.M. Soler, *Int. J. Quantum Chem.* **65**, 453 (1997).
- ¹³N. Troullier, and J.L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
- ¹⁴L. Kleinman, and D.M. Bylander, *Phys. Rev. Lett.* **48**, 1425 (1982).
- ¹⁵S.G. Louie, S. Froyen, and M.L. Cohen, *Phys. Rev. B* **26**, 1738 (1982).
- ¹⁶O.F. Sankey, and D.J. Niklewski, *Phys. Rev. B* **40**, 3979 (1989).
- ¹⁷J. Moreno, and J.M. Soler, *Phys. Rev. B* **45**, 13 891 (1992).
- ¹⁸C. Stampfl, and C.G. Van de Walle, *Phys. Rev. B* **59**, 5521 (1999), and reference therein.
- ¹⁹J.-B. Xia, K.W. Cheah, X.-L. Wang, D.-Z. Sun, and M.-Y. Kong, *Phys. Rev. B* **59**, 10 119 (1999).