PHYSICAL REVIEW B VOLUME 61, NUMBER 12 15 MARCH 2000-II

Native defects and impurities in InN: First-principles studies using the local-density approximation and self-interaction and relaxation-corrected pseudopotentials

C. Stampfl* and C. G. Van de Walle
Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, California 94304

D. Vogel, P. Krüger, and J. Pollmann
Institut für Theoretische Physik II, Festkörperphysik, Universität Münster, D-48149 Münster, Germany

(Received 16 December 1999)

We perform first-principles density-functional calculations to investigate the electronic and atomic structure and formation energies of native defects and selected impurities (O, Si, and Mg) in InN. For *p*-type material, the nitrogen vacancy has the lowest formation energy. In *n*-type material all defect formation energies are high. We discuss the effect of the band-gap underestimate in density functional theory (DFT), and compare the defect electronic structure obtained using DFT (in the local-density approximation, LDA) with a recently developed self-interaction and relaxation-corrected (SIRC) pseudopotential treatment. The SIRC calculations affect the positions of some of the defect states in the band gap, but the general conclusions obtained from the standard DFT-LDA calculations remain valid.

Indium nitride is the least studied of the group-III-nitride materials, which are currently under intense investigation. Bulk InN is difficult to prepare due to its low thermal stability;[1] reliable experimental information about the properties of InN is therefore scarce. Indium-containing nitride alloys are an important constituent in devices: for example, the active layer in short-wavelength light-emitting diodes and laser diodes usually consists of $In_xGa_{1-x}N$. Not intentionally doped InN has often been found to have very high electron densities—an observation similar to GaN before better doping control of that material was achieved. The unintentional *n*-type conductivity of InN has been attributed to the nitrogen vacancy (V_N) or to the nitrogen antisite.[2] In order to control the material properties and ultimately the device characteristics, an understanding of native defects and impurities in the III nitrides and their alloys is essential. The calculations reported here show that neither vacancies nor antisites can explain the observed *n*-type conductivity of InN. We have therefore examined oxygen and silicon impurities, finding that they act as donors and that they can easily be incorporated during growth.

First-principles calculations based on density functional theory (DFT) within the local density approximation (LDA) have produced important information about defects and impurities in semiconductors in general, and the nitrides in particular.[3,4] It is well known, however, that DFT-LDA produces band gaps significantly smaller than experiment.[5] Defects can introduce levels in the band gap; when these levels are occupied with electrons, they contribute to the total energy of the system. If the energetic position of the defect levels is incorrect due to the band-gap error, the resulting total energy may also be affected. The band-gap error results largely from a discontinuity in the exchange-correlation potential upon addition of an extra electron.[6] This discontinuity is inherent to the Kohn-Sham treatment of DFT; indeed, we have found that use of the generalized gradient approximation (GGA) offers no improvement over LDA with respect to the band-gap problem.[7]

No method is currently available that goes beyond DFT and provides total-energy capability for the large supercell calculations required to investigate defects. Even approaches aimed solely at calculating the band structure, such as with the *GW* approach,[8] are currently prohibitively expensive for large cells. A promising approach which yields bulk band structures in good agreement with experiment was recently introduced, based on self-interaction and relaxation-corrected (SIRC) pseudopotentials.[9] The ability of the SIRC potential to produce considerably better band structures than DFT-LDA may reflect an extra nonlocality in the SIRC pseudopotential, related to the nonlocality or orbital dependence in the SIC all-electron potential. In addition, it may mimic some of the energy and the nonlocal space dependence of the self-energy-operator occurring in the *GW* approximation of the electronic many body problem.

The focus of the work reported here is the use of these SIRC potentials to perform calculations of the electronic structure of bulk InN and of various native point defects. InN was chosen because the band-gap problem is particularly severe in this material; indeed, certain pseudopotentials even produce a *negative* band gap within the LDA, and it is likely that the exact Kohn-Sham gap is much smaller than the experimental gap. It should be emphasized that the closure of the gap occurs only near the Γ point, affecting only a very small portion of the Brillouin zone; at the special **k** points used for reciprocal-space integrations the material still behaves like a semiconductor. Still, a critical examination of the DFT-LDA results is appropriate, and the present comparison with the SIRC results allows us to gain insight into the effect of band-gap errors on defect properties. To our knowledge, this is the first work that reports the electronic structure of point defects employing self-interaction corrections. Our comparison between LDA and SIRC allows us to confirm that our conclusions about native defects are not affected by the computational approach.

Our DFT-LDA calculations are carried out using the pseudopotential plane-wave method[10] in a supercell geom-

0163-1829/2000/61(12)/7846(4)/$15.00

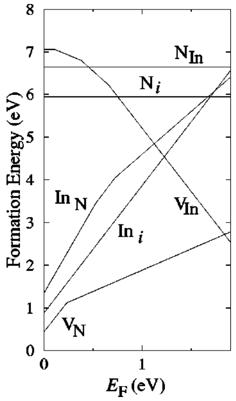

FIG. 1. Calculated native point defect formation energies as a function of the Fermi level for zinc-blende InN under indium-rich conditions. $E_F = 0$ corresponds to the valence-band maximum.

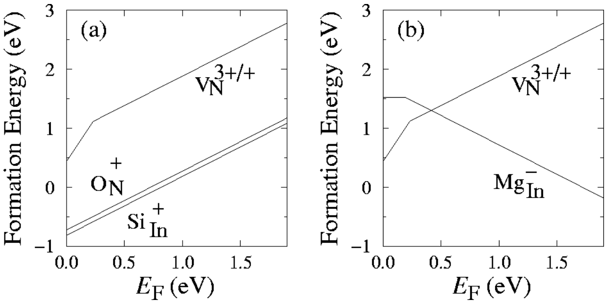

FIG. 2. Defect formation energies of the nitrogen vacancy and impurities in zinc-blende InN as a function of the Fermi level under indium-rich conditions. (a) O and Si and (b) Mg. $E_F = 0$ corresponds to the valence-band maximum.

etry. We use Troullier-Martins pseudopotentials,[11] treating the indium $4d$ electrons with the nonlinear core correction (nlcc),[12] and using an energy cutoff of 40 Ry. We have also performed calculations including the $4d$ electrons as valence states, as well as GGA calculations. The deviations from the LDA/nlcc results are small and do not change our conclusions. We use 32-atom zinc-blende supercells and two special **k** points. Formation energies of defects and impurities in the *wurtzite* phase are similar to the zinc-blende phase, except for interstitial configurations, where the geometry of the wurtzite phase leads to higher formation energies.[13]

The *formation energy* of a defect is a key quantity in our approach;[14,15] defects with low formation energies will occur in high concentrations. We illustrate the definition of the formation energy with the example of a nitrogen vacancy in charge state q, V_N^q:

$$E^f(V_N^q) = E^{\text{tot}}(V_N^q) - E^{\text{tot}}_{\text{bulk}} + \mu_N + qE_F . \tag{1}$$

$E^{\text{tot}}(V_N^q)$ is the total energy of a supercell containing the defect, and $E^{\text{tot}}_{\text{bulk}}$ is the total energy of a supercell of corresponding size, containing only bulk material. The nitrogen atom that is removed from the crystal is placed in a reservoir, the energy of which is the nitrogen chemical potential μ_N. To achieve a given charge state, q electrons need to be taken from the defect and transferred to the reservoir of electrons, which has an energy E_F (the chemical potential of electrons or Fermi level). The zero of E_F is chosen at the valence-band maximum (VBM). Expressions for formation energies of other defects and impurities may be written down in analogy with Eq. (1). A general expression was given and discussed in Ref. 4.

In a compound semiconductor such as InN, the chemical potentials μ_{In} and μ_N are not *a priori* fixed. For purposes of displaying our results, we choose In-rich conditions, setting μ_{In} equal to the energy of bulk In and using the energy of bulk InN to determine μ_N (assuming equilibrium: $\mu_{\text{In}} + \mu_N = \mu_{\text{InN}}$). General conditions can be examined by referring back to the expression for formation energies.

In Fig. 1 the DFT-LDA defect formation energies for the relevant charge states are shown as a function of the Fermi level. Here, E_F spans the experimental band gap of wurtzite InN (1.9 eV). V_N has by far the lowest formation energy of all defects, for all values of the Fermi energy. V_N behaves as a donor which can donate one, two, or three electrons; we find that only the V_N^+ and V_N^{3+} charge states are stable. The V_N^{2+} state is unstable, thus presenting a negative-U effect. Similar behavior of V_N has been found in GaN (Ref. 4) and AlN.[13] The nitrogen vacancy V_N^{3+} has a low formation energy under p-type conditions (E_F low in the gap); it therefore acts as a compensating center in p-type InN (and InGaN alloys). Under n-type conditions (E_F high in the gap) V_{In}^{3-} and V_N^+ have the lowest formation energies. These energies, however, are large (>2.0 eV for $E_F > 1.1$ eV), indicating that n-type InN contains only very small concentrations of these native defects; nitrogen vacancies thus cannot be responsible for the observed n-type conductivity of as-grown InN. The formation energies of the other native defects are all higher than those of the vacancies. For these high-energy defects we did not investigate all possible charge states since the formation energies are clearly prohibitively high. We can thus also rule out antisite defects as being responsible for n-type conductivity.

When used in light emitting devices, the $In_xGa_{1-x}N$ active layer is not strictly required to be doped. Silicon doping of $In_xGa_{1-x}N$ wells of barriers has been used, however, to improve structural and optoelectronic characteristics of the active layer. *Unintentional* doping of $In_xGa_{1-x}N$ may also occur due to the presence of contaminants (oxygen), or of the dopants used for GaN and AlGaN cladding and confinement layers. An investigation of the incorporation of impurities in InN is therefore important; here we studied the O, Si, and Mg impurities. Silicon is commonly used to achieve n-type conductivity in GaN and $Al_xGa_{1-x}N$, O is a common unintentional dopant (contaminant), and Mg is used to achieve p-type doping. The O, Si, and Mg chemical potentials are assumed to be determined by thermal equilibrium with Al_2O_3, Si_3N_4, and Mg_3N_2, respectively.

In Fig. 2(a) we show the formation energies of the O and Si impurities in InN. Oxygen occupies a nitrogen site, and silicon an indium site; both act as donors. We also include the formation energy of V_N for comparison. The formation energies of O and Si are low, indicating that these impurities will be readily incorporated during growth. The results also indicate that there will be no compensation of these impurities by acceptor-type native defects. n-type doping of InN (and InGaN alloys) should therefore be easily attainable. This behavior is similar to what has been found in GaN.[3,16]

Figure 2(b) shows the formation energy for Mg on an In

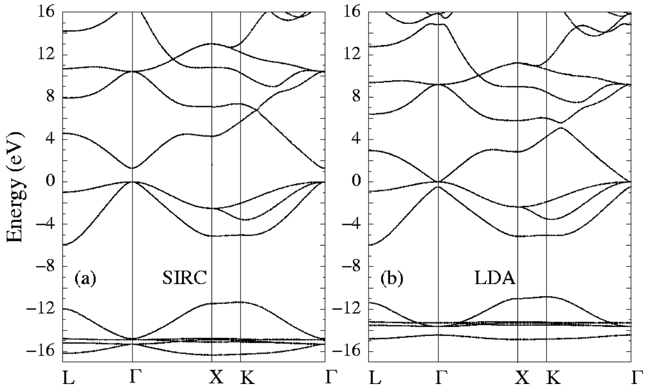

FIG. 3. Electronic band structure of zinc-blende InN as obtained using (a) the SIRC pseudopotentials of Ref. 9 (using a 150 Ry cutoff), and (b) ''regular'' LDA pseudopotentials of Troullier-Martins, Ref. 11 (using an 80 Ry cutoff).

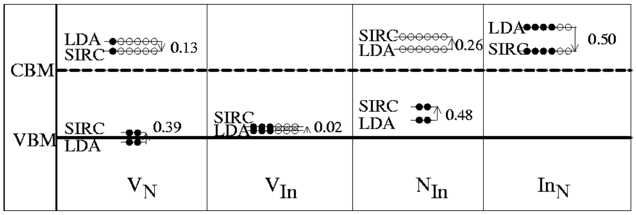

FIG. 4. Schematic diagram of defect-induced levels (in eV), based on Kohn-Sham eigenvalues, showing a comparison between LDA and SIRC calculations. States above the conduction-band minimum are placed at an energy above the dashed line, corresponding to the calculated energy difference between the defect level and the conduction-band minimum within LDA and SIRC, respectively.

site. The position of the acceptor level (i.e., the transition between neutral and negative charge states) is at about 0.2 eV. For comparison, in GaN (Ref. 17) and AlN (Ref. 13) the acceptor levels are at about 0.2 eV and 0.4 eV, respectively. The formation energy of Mg in InN is lower than in GaN, indicating high solubility for Mg in InGaN. Just like in GaN, nitrogen vacancies are a potential source of compensation in Mg-doped InN and InGaN alloys.

We now examine the effect of the DFT-LDA band-gap problem on native-defect properties by using SIRC pseudopotentials. For this purpose, we have investigated vacancies and antisites. We used the pseudopotentials as parametrized in Ref. 9, which include the In-4*d* electrons as valence electrons. We carefully tested convergence as a function of energy cutoff, and found that at least 100 Ry is required.

The SIRC electronic band structure of zinc-blende InN is shown in Fig. 3(a). The band gap has a value of ≈1.3 eV, a significant improvement over the standard LDA (and GGA) pseudopotential result [compare Fig. 3(b)] which is negative. For InN in the *wurtzite* structure, calculated at the experimental lattice constant, a band gap of 1.55 eV is obtained in excellent agreement with our previous work in which a localized basis was used.[9] For calculating the electronic structure of the native defects using the SIRC pseudopotentials, the relaxed atomic geometry was taken from our calculations using the Troullier-Martins pseudopotentials including the 4*d* electrons as valence. Only neutral charge states were considered.

Figure 4 illustrates the level positions in or near the band gap for vacancies and antisites, as obtained from Kohn-Sham eigenvalues. The position of localized states was obtained by averaging over special **k** points. Defect levels should, strictly speaking, be obtained by considering energy differences between different charge states;[4] however, an inspection of the Kohn-Sham eigenvalues is very informative and suffices for the purposes of our study. Figure 4 shows the level positions of the vacancies and the antisites on relative energy scales with respect to the appropriate VBM or conduction-band minimum (CBM).

For V_N, using the SIRC pseudopotentials, there is a doubly occupied singlet state just above the VBM, and a singly occupied triplet state above the CBM. This is qualitatively similar to what we found for the LDA calculations, but with the important quantitative difference that conduction-band states (including the defect-induced triplet state) are shifted up in energy. This feature is illustrated in Fig. 4 by referencing the defect-induced levels with respect to the CBM. For states above the CBM, we focus on the energy difference between the defect level and the CBM, calculated within LDA and SIRC. This energy difference is then used to determine the position of the defect level above the CBM in Fig. 4. For ease of display and comparison, this CBM is shown as a single (dashed) line, even though the LDA and SIRC band gaps are obviously quite different.

The fact that defect levels above the CBM shift upward with the conduction band is a very important finding. The shift confirms that V_N acts as a shallow donor, even when a band-gap correction is applied. The observation that LDA and SIRC defect levels exhibit a shift very similar to that of the CBM indicates that the triplet level exhibits mainly conduction-band character. The singlet state near the VBM is also shifted to higher energy, but by an amount (0.39 eV) much smaller than the band-gap correction. An inspection of the wave functions of the defect-induced states indicated that they are very similar in SIRC and LDA.

The SIRC approach currently does not allow evaluation of total energies. Still, we can attempt to estimate how the calculated changes in the band structure affect the total energy; such an estimate is necessarily crude, since the effect of a shift in an occupied level should really be evaluated *self-consistently*. Nonetheless, we can draw some important qualitative conclusions. For V_N^0, the total energy should reflect the shift in the conduction-band-related triplet state (i.e., an increase in the formation energy of V_N^0). This contribution to the energy is absent for V_N^+. For both V_N^0 and V_N^+, the shift of the occupied singlet state near the VBM would tend to increase the total energy by a small amount.

Turning now to the indium vacancy, this defect creates a fully occupied singlet in the valence-band continuum, and a triplet state close to the VBM which is occupied by three electrons and can be filled with three more electrons, i.e., it is a triple acceptor. The position of this state with respect to the VBM only shifts by 0.02 eV in SIRC compared to LDA.

The nitrogen antisite creates an occupied singlet state in the band gap, as well as a higher-lying triplet state which can trap six electrons. In the SIRC calculations, the singlet state is higher in the band gap by about 0.5 eV. This implies a higher formation energy of this defect than obtained with the LDA calculations. Since the LDA energy was already so high as to imply very small concentrations, this correction would not change our conclusions. The empty triplet state essentially follows the CBM; since it is empty, however, it also does not affect the formation energy of the neutral defect.

For the indium antisite, finally, we find from DFT-LDA that a triplet level, occupied by four electrons, is introduced above the CBM. The SIRC calculations show that this level shifts upwards with respect to the VBM, but by an amount smaller than the shift in the CBM; still, the level remains well above the CBM, and the formation energy would be higher than determined by the LDA calculations. Again, since the latter is already prohibitively high, our conclusions based on LDA remain valid.

In summary, the nitrogen vacancy is found to be the lowest energy native defect in InN, acting as a potential source of compensation in *p*-type material. In *n*-type InN, the formation energies of all native defects are high, excluding them as a source of *n*-type conductivity in as-grown material. Oxygen and silicon act as donors, with formation energies significantly lower than V_N. We compared the defect electronic structure of selected native defects as obtained by DFT-LDA with self-interaction and relaxation-corrected (SIRC) calculations. The character of the defect-induced states is very similar in SIRC calculations compared to DFT-LDA, but conduction-band related states are shifted to higher energies. This may affect total energies in some instances, but for the present system these findings do not alter conclusions based on the DFT-LDA calculations.

This work was supported in part by DARPA under Contract No. MDA972-95-3-0008. C.S. gratefully acknowledges support from the DFG (Deutsche Forschungsgemeinschaft) and fruitful discussions with Martin Fuchs and Jörg Neugebauer. The Münster group acknowledges financial support from the DFG under Grant No. Po 215/12-1,2.

---

*Present address: Department of Physics and Astronomy, Northwestern University, Evanston, IL 60208, and Fritz-Haber-Institut, Berlin, Germany.

[1] *Properties of Group III-Nitrides*, edited by J. H. Edgar, EMIS Datareviews Series (EMIS, London, 1994).

[2] T. L. Tansley and C. P. Foley, J. Appl. Phys. **60**, 2092 (1986); M. Sato, Jpn. J. Appl. Phys., Part 2 **36**, L658 (1997).

[3] J. Neugebauer and C. G. Van de Walle, Phys. Rev. B **50**, 8067 (1994).

[4] J. Neugebauer and C. G. Van de Walle, Adv. Solid State Phys. **35**, 25 (1996).

[5] J. P. Perdew and M. Levy, Phys. Rev. Lett. **51**, 1884 (1983); L. J. Sham and M. Schlüter, *ibid.* **51**, 1888 (1983).

[6] R. W. Godby, M. Schlüter, and L. J. Sham, Phys. Rev. B **37**, 10 159 (1988).

[7] C. Stampfl and C. G. Van de Walle, Phys. Rev. B **59**, 5521 (1999).

[8] M. S. Hybertsen and S. G. Louie, Phys. Rev. B **34**, 5390 (1986).

[9] D. Vogel, P. Krüger, and J. Pollmann, Phys. Rev. B **55**, 12 836 (1997), and references therein.

[10] M. Bockstedte, A. Kley, J. Neugebauer, and M. Scheffler, Comput. Phys. Commun. **107**, 187 (1997).

[11] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[12] S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B **26**, 1738 (1982).

[13] C. Stampfl and C. G. Van de Walle, Appl. Phys. Lett. **72**, 459 (1998); Mater. Res. Soc. Symp. Proc. **482**, 905 (1998).

[14] S. B. Zhang and J. E. Northrup, Phys. Rev. Lett. **67**, 2339 (1991).

[15] D. B. Laks, C. G. Van de Walle, G. F. Newmark, P. E. Blöchl, and S. T. Pantelides, Phys. Rev. B **45**, 10 965 (1992).

[16] J. Neugebauer and C. G. Van de Walle, *Proceedings ICPS-22* (World Scientific, Singapore, 1995), p. 2327.

[17] J. Neugebauer and C. G. Van de Walle, Appl. Phys. Lett. **68**, 1829 (1996).