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CALCULATIONS OF NATIVE DEFECTS AND IMPURITIES IN CUBIC GaN INCLUDING HIGH PRESSURE EFFECTS

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Using the Green-function matrix technique based on the linear muffin-tin orbital method in the atomic-spheres approximation we perform self-consistent calculations of the electronic structure for native defects and impurities in cubic GaN. Native defects as N and Ga vacancies and antisites and substitutional impurities: Zn, C and Ge in different charge states are investigated. Resulting positions of the defect levels are compared with tight-binding and pseudopotential calculations. High pressure behavior is also studied in comparison with some other theoretical and experimental data.

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The blue electroluminescence characteristic of GaN has been of interest over a number of years [1]. Applications require an understanding of the nature of native defects, in particular the charge states and energies of electron levels generated by: gallium vacancy V_{Ga} , nitrogen vacancy V_{N} , and antisites: Ga_{N} and N_{Ga} — defects likely to persist even under optimal growth conditions.

In this paper we concentrate on native defects in GaN and on the most common dopant in GaN, which is Zn. Our purpose is to find energy positions of the defect levels at ambient and at high hydrostatic pressure.

GaN can be grown in two phases, the cubic and wurtzite phase. We focus here on the cubic one believing that there is no substantial difference in impurity level positions between these two phases and conclusions arising from the present calculations can be applied to wurtzite phase as well.

Calculations are performed with the “first-principles” linear-muffin-tin-orbital (LMTO) Green function method [2]. This method is based on the local-density approximation (LDA) [3]. The fundamental gaps obtained by using LDA are generally too small. This is overcome by rigidly shifting the conduction bands upwards (the “scissors operator”).

The valence electronic structure of the impurity atom is obtained from the solid Green function G , which is found by solving the Dyson equation: $G = G^0 + G^0 \Delta V G$, where G^0 is the Green function of the pure crystal host and ΔV — the perturbation due to the impurity. In the LMTO method the host Green function is calculated from the band structure of the pure crystal with the atomic sphere approximation (ASA), i.e., the crystal volume is approximated by slightly overlapping atom centered spheres, inside which the potential is taken spherically symmetric. In zinc-blende structure additional “empty” spheres are introduced [4]. In this work we consistently choose all spheres to have the same size determined by the experimental host lattice constant. The impurities considered are all ideal substitutional ones, i.e., no relaxation of the neighboring atoms is allowed for.

At first we will discuss the levels introduced by the native defects comparing our results with some experimental data [5–9]. In Fig. 1 the calculated positions of defect levels in neutral and charged states are indicated.

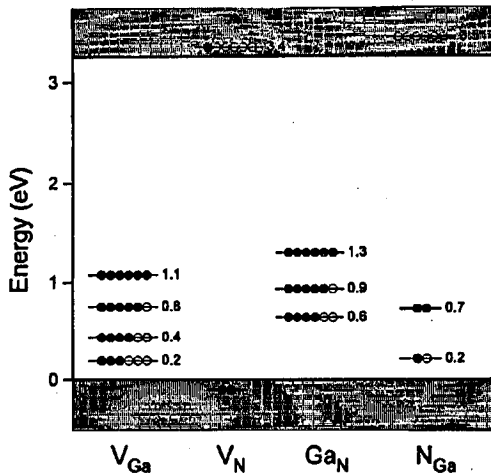


Fig. 1. Distribution of defect levels for the gallium and nitrogen vacancies and antisites. The occupations are shown for the different charge states (filled circles are electrons, open circles are holes).

The level at 0.1–0.2 eV above valence band (v.b.) edge has been identified by photoluminescence of doped single crystal GaN [1, 9] to be a result of gallium vacancy, V_{Ga} . Our value for the neutral charge state, 0.2 eV, agrees very well with this prediction and also with the tight-binding (TB) calculations [10] and with the recent pseudopotential results (0.3 eV) [11].

The shallow donor levels have been ascribed [8] to nitrogen vacancy. As results from the present calculations the s -like state of V_N lies as a resonance below v.b. edge, whereas the p -like state forms a resonance in the conduction band (c.b.). For the neutral charge state the one electron occupying this resonance state is transferred to bottom of c.b. forming an effective mass state — the nitrogen vacancy acts as a single donor. The above result agrees qualitatively with the

pseudopotential calculations [11], but our state is lying somewhat lower (about 0.1 eV above c.b. edge, pseudopotential gives value 0.8 eV).

The deep trap (0.7–1.1 eV above v.b.) reported in literature [8] is close to our result for gallium antisite, Ga_N . For the neutral charge state we have got the triplet state in the band gap occupied with four electrons (double acceptor). It lies at 0.6 eV above v.b. in very good agreement with the TB predictions [10], but decidedly lower than the same state obtained by the pseudopotential calculations (1.3 eV [11]).

The position of nitrogen antisite, N_Ga , is controversial — TB [10] gives its position at about 0.5 eV below c.b., whereas pseudopotential calculations [11] lead to quite different value: 0.4 eV above v.b. Our value for neutral charge state, 0.74 eV above v.b., is much closer to that obtained by pseudopotential method.

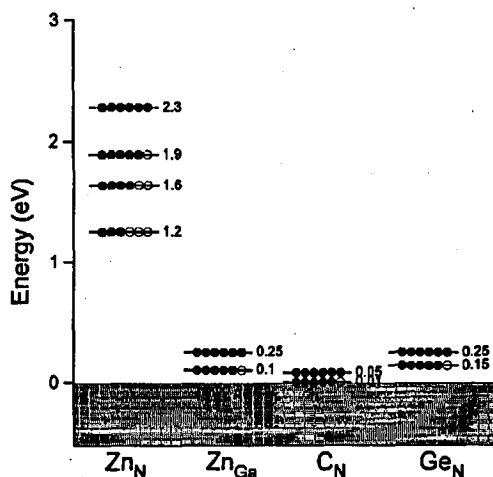


Fig. 2. Distribution of defect levels for the substitutional Zn (on N and Ga sites), C and Ge (on N site) impurities. The occupations are shown for the different charge states (filled circles are electrons, open circles are holes).

The calculated level positions for some substitutional acceptor impurities are shown in Fig. 2. As previously, states with different occupations are presented.

One of the most interesting dopant in GaN is Zn. There are some experimental evidences that Zn introduces several deep states in GaN [12]. The Zn on N site (Zn_N) might be capable of binding up to three electrons introducing deep acceptor-like centers. The positions of these levels (1.2–2.2 eV) obtained by us are somewhat higher than the approximate binding energies estimated from luminescence spectra (0.7–1.4 eV) and connected by the authors [12] with Zn centers or Zn-V_N complexes.

Zn on Ga site (Zn_Ga) forms a shallow acceptor state — our result is 0.25 eV for charged and 0.1 eV for the neutral charge state, in a good agreement with experimental data (0.34 eV [5, 8]).

We have calculated also the level positions for the two other dopants: C and

Ge on the N site. In the both cases we have got the p -like levels — very close to the v.b. edge for the neutral charge states (occupied by one hole and five electrons).

The high pressure behavior was studied in three different cases: (1) resonance in conduction band — V_N , (2) deep donor-like state — N_{Ga} , (3) shallow acceptor — Zn_{Ga} .

For each of these cases we have calculated the energy positions of defect levels at the pressure values: 10, 20 and 24 GPa. The obtained pressure coefficient of the main energy gap is 38 meV/GPa. In the first case (V_N) the resonance state is shifted down in respect of the c.b. minimum with the pressure coefficient 24 meV/GPa (14 meV/GPa up in respect of v.b.) appearing in the band gap at the pressure value of 4 GPa. The pseudopotential calculations [11] estimate the pressure coefficient of the considered level with respect to c.b. to be the same as that of the energy gap.

In the second case, the deep donor-like level coming from N_{Ga} is shifted up with respect to v.b. edge with pressure coefficient 6 meV/GPa (32 meV/GPa down with respect to c.b.).

In the case of the shallow acceptor — Zn_{Ga} , we found that the defect state does not shift with pressure in respect of the v.b., therefore its pressure coefficient in respect of c.b. is 38 meV/GPa, the same as the pressure coefficient of the energy gap, in agreement with experimental finding [13].

Concluding, qualitatively different high pressure behavior is found for three different types of defect states in GaN — resonance in conduction band, deep donor level and shallow acceptor.

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References

- [1] M. Ilegams, R. Dingle, R.A. Logan, *J. Appl. Phys.* **43**, 3797 (1972).
- [2] O. Gunnarson, O. Jepsen, O.K. Andersen, *Phys. Rev. B* **27**, 7144 (1983).
- [3] R.O. Jones, O. Gunnarson, *Rev. Mod. Phys.* **61**, 681 (1989).
- [4] D. Glötzel, B. Segall, O.K. Andersen, *Solid State Commun.* **36**, 403 (1980).
- [5] R. Dingle, M. Ilegams, *Solid State Commun.* **9**, 175 (1971).
- [6] J.C. Veseley, M. Shatzkes, P.J. Burkhardt, *Phys. Rev. B* **10**, 582 (1974).
- [7] V.S. Vavilov, S.I. Makarov, M.V. Chukichev, I.V. Chetverikova, *Sov. Phys. Semicond.* **13**, 2153 (1979).
- [8] T.L. Tansley, R.J. Egan, *Mater. Res. Soc.* **242**, 395 (1992).
- [9] B. Monemar, *Phys. Rev. B* **10**, 676 (1974).
- [10] D.W. Jenkins, J.D. Dow, *Phys. Rev. B* **39**, 3317 (1989).
- [11] P. Bogusławski, to be published.
- [12] B. Monemar, O. Lagerstedt, H.P. Gislason, *J. Appl. Phys.* **51**, 625 (1980).
- [13] H. Teisseyre, P. Perlin, T. Suski, I. Grzegory, J. Jun, S. Porowski, *J. Phys. Chem. Solids* **56**, 353 (1995).