Carbon impurities and the yellow luminescence in GaN

J. L. Lyons, A. Janotti, and C. G. Van de Walle

Carbon impurities and the yellow luminescence in GaN

J. L. Lyons,[a)] A. Janotti, and C. G. Van de Walle
Department of Materials, University of California, Santa Barbara, California 93106-5050, USA

Using hybrid functional calculations we investigate the effects of carbon on the electrical and optical properties of GaN. In contrast to the currently accepted view that C substituting for N (C_N) is a shallow acceptor, we find that C_N has an ionization energy of 0.90 eV. Our calculated absorption and emission lines also indicate that C_N is a likely source for the yellow luminescence that is frequently observed in GaN, solving the longstanding puzzle of the nature of the C-related defect involved in yellow emission. Our results suggest that previous experimental data, analyzed under the assumption that C_N acts as a shallow acceptor, should be re-examined. © *2010 American Institute of Physics.* [doi:10.1063/1.3492841]

GaN and its related alloys already have many commercial applications in blue/green light-emitting diodes and lasers as well as high-frequency transistors.[1,2] Nevertheless, the role of common impurities, such as carbon, in the electrical and optical properties of GaN is still not fully understood.[3–5] C-doped GaN has been used as a semi-insulating buffer layer in AlGaN/GaN heterojunction field-effect transistors,[6,7] yet the microscopic mechanisms that control the conductivity are still unclear. A number of experimental and theoretical studies inferred that C substituting on the N site (C_N) acts as a shallow acceptor,[8–16] and that semi-insulating behavior would result from self-compensation, i.e., the incorporation of the C_N acceptor and the C_{Ga} donor in equal concentrations.[12,15] While some theoretical studies have reported deep levels arising from interstitial carbon,[17] only one theoretical study has reported a deep acceptor level for C_N in GaN.[18]

Carbon has also been associated with the widely observed yellow luminescence (YL) in GaN.[3,12,19,20] As far back as 1980, Ogino and Aoki[19] proposed that the YL was related to carbon and proposed a complex consisting of a gallium vacancy, V_{Ga}, next to C_N. Such a configuration is implausible, however, due to the fact that both V_{Ga} and C_N act as acceptors and are unlikely to bind.[9] A decade later, V_{Ga} in its own right (possibly complexed with O_N donors) was proposed as a source of YL,[9] subsequently supported by extensive experimental evidence.[21–23] It was never claimed or established, however, that V_{Ga} is the *only* possible source of YL in GaN, and various reports have appeared of YL in material that was unlikely to contain V_{Ga} (in particular, semi-insulating material,[22,24] in which the formation energy of V_{Ga} is high and hence their concentration is expected to be negligibly low). In addition, correlations between YL and C concentration have kept appearing.[12–14,24,25] No credible carbon-related configuration that could explain the YL has been identified to date. Due to this lack of understanding, the YL continues to be an undesirable and uncontrolled feature in many optoelectronic devices.

First-principles studies based on density functional theory (DFT) within the local density approximation (LDA) or the generalized gradient approximation (GGA) have consistently reported that C acts as an acceptor when substituting on the N site (with an ionization energy in the range of 200–300 meV) and as a donor on the cation site.[9,10,17,26,27] The problem with the LDA and GGA in the DFT calculations is the large uncertainty in the position of impurity levels due to the severe underestimation of band gaps, as well as a tendency to underestimate localization. As we have recently shown in the case of N-doped ZnO,[28] calculations based on hybrid functionals overcome these problems and can lead to dramatically different physics that explains experimental results.

In this letter, we demonstrate, based on hybrid functional calculations, that (1) C_N is *not* a shallow acceptor but a very *deep* acceptor with an ionization energy of 0.90 eV; and (2) the C_N center itself is the source of the YL that has been widely observed in C-containing material. The optical absorption and emission characteristics of this C_N center match the experimental data, showing very good agreement with configuration coordinate diagrams derived based on experimental observations.[13,19]

Our calculations are based on the generalized Kohn–Sham scheme[29] with the hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE) (Ref. 30) as implemented in the VASP code.[31] In the HSE method, the exchange potential is divided in short-range and long-range parts with a screening length of 10 Å. In the short-range part, a fraction of nonlocal Hartree–Fock exchange potential is mixed with the GGA exchange potential of Perdew, Burke, and Ernzerhof (PBE).[32] The long-range part and the correlation potential are described by the PBE functional. The mixing parameter for the Hartree–Fock potential is set to 0.31, resulting in a band gap of 3.5 eV that is in good agreement with the experimental value.[33] We treat the Ga 3d electrons as core states through the projector-augmented wave method.[34,35] Our tests indicate that all the properties discussed here are independent of inclusion of the d electrons as valence states. The calculated lattice parameters $a=3.20$ Å, $c=5.20$ Å, and $u=0.38$ for wurtzite GaN are in good agreement with experiment.[33] The impurity calculations are performed using a 96-atom supercell, a plane-wave basis set with a 300 eV cutoff, and a $2\times2\times2$ Monkhorst–Pack k-point set. Based on tests using larger supercells, errors of less than 0.1 eV in formation energies and transition levels are expected.

The likelihood of incorporating an impurity in a crystal is determined by its formation energy. In the case of C on the

---

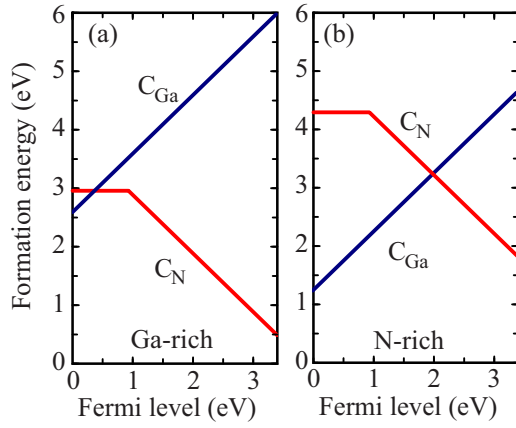a)Electronic mail: jllyons@engineering.ucsb.edu.

FIG. 1. (Color online) Formation energy vs Fermi level for C_{Ga} and C_N in GaN. Ga-rich conditions are shown in (a) and N-rich conditions in (b).
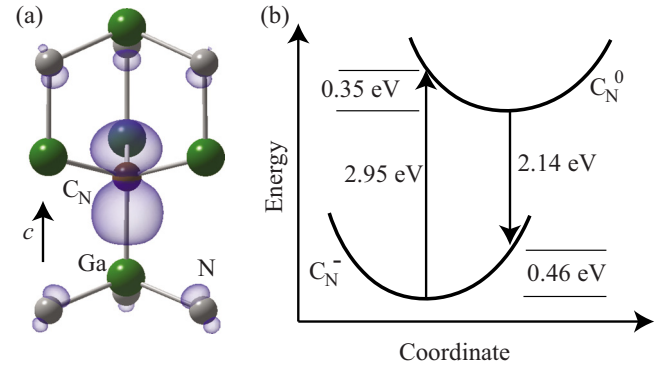

FIG. 2. (Color online) (a) Spin density of C_N^0, with an isosurface at 10% of the maximum. (b) Configuration-coordinate diagram for the C_N impurity in GaN. The coordinate corresponds to the distance between C and Ga along the c axis. Optical absorption with C_N^- as the initial state occurs starting at 2.60 eV and peaks at 2.95 eV. Emission associated with the $C_N^0 \rightarrow C_N^-$ transition is predicted to occur at 2.14 eV, i.e., in the yellow region of the spectrum.

N site in GaN, the formation energy is given by the following:[36]

$$E^f(C_N^q) = E_{tot}(C_N^q) - E_{tot}(\text{GaN}) - \mu_C + \mu_N$$
$$+ q(E_F + \epsilon_v + \Delta V), \qquad (1)$$

where $E_{tot}(C_N^q)$ is the total energy of the crystal containing one C_N in charge state q in the supercell, and $E_{tot}(\text{GaN})$ is the total energy of a perfect crystal in the same supercell. The N atom that is removed from the crystal is placed in a reservoir of energy μ_N, referenced to the energy of an isolated N_2 molecule. The chemical potential μ_N can vary over a range determined by the GaN formation enthalpy [calculated to be $\Delta H_f(\text{GaN}) = -1.34$ eV], reflecting growth conditions that can vary from N-rich to Ga-rich. The C atom that is added is taken from a reservoir with energy μ_C; for purposes of displaying our results we set μ_C equal to the energy per atom in the diamond crystal. The last term in Eq. (1) represents the energy of the electron reservoir; E_F is the Fermi level, referenced to the bulk valence-band maximum (VBM) ϵ_v; ΔV is the alignment of the averaged electrostatic potential in the bulk and in a region far from the impurity in the impurity-containing supercell.

Carbon can incorporate either on the Ga or N sites in GaN. Carbon on interstitial sites has been reported to have high formation energies and is therefore not discussed in the present work.[17,26] From atomic-size considerations, C is expected to be most stable on the N site. However, Fig. 1 shows that the site preference depends on the relative abundance of Ga and N, i.e., on the Ga and N chemical potentials, as well as on the Fermi level.

Consistent with previous reports,[17,26] we find that C_{Ga} acts as a shallow donor. The extra electron from the C impurity occupies a conduction-band state that has been perturbed by the presence of the impurity. The size mismatch between C and Ga leads to a very large local lattice relaxation around C_{Ga}: the four nearest-neighbor N atoms relax inward by 26% of the N–Ga bond length. We explored possible off-site displacements and found that a DX-like C_{Ga}^- configuration in which C_{Ga}^- is significantly displaced along the c axis is stable only for E_F values well above the conduction-band minimum (CBM).

Our findings for C_N contrast with those of previous studies based on DFT in the LDA or GGA, which found C_N to be a shallow acceptor.[9,10,17,26,27] Our hybrid functional results

show that it is actually a *deep* acceptor with the $\epsilon(0/-)$ charge-state transition level at 0.90 eV above the VBM (see Fig. 1). In the negative charge state (C_N^-), the four nearest-neighbor Ga atoms relax inward by just 2% of the equilibrium N–Ga bond length. In the neutral charge state (C_N^0), an asymmetric distortion occurs in which the C–Ga bond along the c axis becomes 8% longer, while the other three C–Ga bonds are only 1% longer. The spin density of C_N^0 is shown in Fig. 2(a). We find it to be oriented axially along the c direction, toward one of the nearest-neighbor Ga atoms. This result could in principle be verified by electron paramagnetic resonance experiments.

Considering that the VBM in GaN is derived mostly from N p states, the position of the $\epsilon(0/-)$ transition level is consistent with the fact that the C atomic p states are significantly higher in energy than the N p states. This is analogous to the effect of N substituting for O in ZnO, in which case N leads to a deep acceptor level at 1.3 eV above the VBM.[28]

Because of the large difference in lattice relaxations around C_N^- and C_N^0, the $\epsilon(0/-)$ transition level is expected to differ significantly from the level for optical transitions, which occur on a time scale much shorter than atomic relaxation and leave the atomic configuration of the initial state unchanged. Optical absorption and emission energies can be obtained by inspecting the calculated configuration coordinate diagram shown in Fig. 2(b). Starting from C_N^- as the initial state, absorption of a photon excites an electron to the CBM, leaving C_N in the neutral charge state. The absorption peak is predicted to occur at 2.95 eV (vertical transition, in which the atomic configuration is fixed to that of C_N^-), with an onset at 2.60 eV. The subsequent emission, in which an electron in the conduction band (or bound to a shallow donor) is transferred to C_N^0, resulting in C_N^-, peaks at 2.14 eV, with a Franck–Condon shift of 0.46 eV. The Stokes shift, i.e., the difference between the absorption and emission peaks, is therefore equal to 0.81 eV. The calculated configuration coordinate diagram in Fig. 2(b) bears a remarkable resemblance to published diagrams based on experimental results,[13,19] strengthening our proposal that C_N is the source of C-related YL.

This relatively broad emission at 2.14 eV related to C_N solves the longstanding mystery related to the microscopic identity of the C-related center that gives rise to YL in GaN. We are *not* arguing here that C_N is the *only* source of yellow luminescence in GaN; Ga vacancies and related complexes have been demonstrated to give rise to YL as well.[9,21–23] However, there is undeniable evidence in the literature[12–14,25] about a correlation between carbon and YL, for which we now provide a microscopic explanation. The possibility that C_N would be the source of the YL had never been seriously considered, because of the belief that C_N acted as a shallow acceptor. This of course now raises the question as to the origin of the experimental features that had been interpreted to be signatures of a shallow acceptor in C-doped samples. The carbon impurity could, in principle, participate in a complex that gives rise to shallower transition levels but our extensive investigations have not revealed any candidates. The resolution of that issue is beyond the scope of this work but some of the suggestions that were discussed in our investigation of nitrogen acceptors in ZnO (Ref. 28) may apply in this case as well; e.g., luminescence due to stacking faults being mistaken for a shallow-acceptor line.

In summary, we have reported results of hybrid functional calculations for the C impurity in GaN. We find that C_N is a deep acceptor in GaN, in contrast to previous reports. C_N gives rise to a broad optical emission line peaked at 2.14 eV, and thus explains the YL observed in C-doped GaN samples.

[1] S. Pimputkar, J. S. Speck, S. P. DenBaars, and S. Nakamura, Nat. Photonics **3**, 180 (2009).
[2] U. K. Mishra, P. Parikh, and Y. F. Wu, Proc. IEEE **90**, 1022 (2002).
[3] *Gallium Nitride (GaN) I*, Semiconductors and Semimetals Vol. 50, edited by J. I. Pankove and T. D. Moustakas (Academic, San Diego, 1998); *Gallium Nitride (GaN) II*, Semiconductors and Semimetals Vol. 57, edited by J. I. Pankove and T. D. Moustakas (Academic, San Diego, 1999).
[4] E. R. Glaser, W. E. Carlos, G. C. B. Braga, J. A. Freitas, W. J. Moore, B. V. Shanabrook, A. E. Wickenden, D. D. Koleske, R. L. Henry, M. W. Bayerl, M. S. Brandt, H. Obloh, P. Kozodoy, S. P. DenBaars, U. K. Mishra, S. Nakamura, E. Haus, J. S. Speck, J. E. Van Nostrand, M. A. Sanchez, E. Calleja, A. J. Ptak, T. H. Myers, and R. J. Molnar, Mater. Sci. Eng., B **93**, 39 (2002).
[5] H. Morkoç, *Handbook of Nitride Semiconductors and Devices* (Wiley, New York, 2008), Vol. 1–3.
[6] C. Poblenz, P. Waltereit, S. Rajan, S. Heikman, U. K. Mishra, and J. S. Speck, J. Vac. Sci. Technol. B **22**, 1145 (2004).
[7] A. Armstrong, A. R. Arehart, B. Moran, S. P. DenBaars, U. K. Mishra, J. S. Speck, and S. A. Ringel, Appl. Phys. Lett. **84**, 374 (2004).
[8] S. Fischer, C. Wetzel, E. E. Haller, and B. K. Meyer, Appl. Phys. Lett. **67**, 1298 (1995).
[9] J. Neugebauer and C. Van de Walle, Appl. Phys. Lett. **69**, 503 (1996).
[10] P. Bogusławski and J. Bernholc, Phys. Rev. B **56**, 9496 (1997).
[11] D. J. As and U. Köhler, J. Phys.: Condens. Matter **13**, 8923 (2001).
[12] C. H. Seager, A. F. Wright, J. Yu, and W. Götz, J. Appl. Phys. **92**, 6553 (2002).
[13] A. Armstrong, A. R. Arehart, D. S. Green, U. K. Mishra, J. S. Speck, and S. A. Ringel, J. Appl. Phys. **98**, 053704 (2005).
[14] D. S. Green, U. K. Mishra, and J. S. Speck, J. Appl. Phys. **95**, 8456 (2004).
[15] A. Armstrong, C. Poblenz, D. S. Green, U. K. Mishra, J. S. Speck, and S. A. Ringel, Appl. Phys. Lett. **88**, 082114 (2006).
[16] M. A. Reshchikov and H. Morkoç, J. Appl. Phys. **97**, 061301 (2005).
[17] A. F. Wright, J. Appl. Phys. **92**, 2575 (2002).
[18] V. Fiorentini, L. F. Bernardini, A. Bosin, and D. Vanderbilt, *Proceedings of the 23rd International Conference on Physics of Semiconductors* (World Scientific, Singapore, 1996), Vol. 4, p. 2877.
[19] T. Ogino and M. Aoki, Jpn. J. Appl. Phys. **19**, 2395 (1980).
[20] S. O. Kucheyev, M. Toth, M. R. Phillips, J. S. Williams, C. Jagadish, and G. Li, J. Appl. Phys. **91**, 5867 (2002).
[21] K. Saarinen, T. Laine, S. Kuisma, J. Nissilä P. Hautoj ärvi, L. Dobrzynski, J. M. Baranowski, K. Pakula, R. Stepniewski, M. Wojdak, A. Wysmolek, T. Suski, M. Leszczynski, I. Grzegory, and S. Porowski Phys. Rev. Lett. **79**, 3030 (1997).
[22] R. Armitage, W. Hong, Y. Qing, H. Feick, J. Gebauer, E. R. Weber, S. Hautakangas, and K. Saarinen, Appl. Phys. Lett. **82**, 3457 (2003).
[23] A. Sedhain, J. Li, J. Y. Lin, and H. X. Jiang, Appl. Phys. Lett. **96**, 151902 (2010).
[24] F. Reurings and F. Tuomisto, Proc. SPIE **6473**, 64730M (2007).
[25] R. Zhang and T. F. Kuech, Appl. Phys. Lett. **72**, 1611 (1998).
[26] L. E. Ramos, J. Furthmüller, J. R. Leite, L. M. R. Scolfaro, and F. Bechstedt, Phys. Status Solidi B **234**, 864 (2002).
[27] T. A. G. Eberlein, R. Jones, S. Öberg, and P. R. Briddon, Appl. Phys. Lett. **91**, 132105 (2007).
[28] J. L. Lyons, A. Janotti, and C. G. Van de Walle, Appl. Phys. Lett. **95**, 252105 (2009).
[29] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[30] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003).
[31] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[32] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[33] *Semiconductors: Basic Data*, 2nd ed., edited by O. Madelung (Springer, Berlin, 1996).
[34] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
[35] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[36] C. G. Van de Walle and J. Neugebauer, J. Appl. Phys. **95**, 3851 (2004).