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Buckeridge et al. Reply

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DOI:
10.1103/PhysRevLett.115.029702

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Document Version
Publisher's PDF, also known as Version of record

Citation for published version (Harvard):
Buckeridge, J, Catlow, CRA, Scanlon, DO, Keal, TW, Sherwood, P, Miskufova, M, Walsh, A, Woodley, SM & Sokol, AA 2015, 'Buckeridge et al. Reply', *Physical Review Letters*, vol. 115, no. 2, 029702.
https://doi.org/10.1103/PhysRevLett.115.029702

Link to publication on Research at Birmingham portal

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Download date: 03. May. 2024

Buckeridge *et al.* Reply: In our Letter [1], we have investigated the stability of holes in GaN, at the valence band maximum (VBM) or trapped by Mg or other impurities. We showed that (1) free holes are less thermodynamically stable than nitrogen vacancies (V_N), and (2) impurity-hole binding energies in the dilute limit are too high to be overcome by mere thermal treatments.

These conclusions are supported by and rationalize experiments on GaN doped with divalent metals in low concentrations, which remains universally n type—no doping strategies result in observable minority carrier concentrations [2–4], contradicting the claims made in Ref. [5]. If Ref. [5] were correct, then GaN p-n junctions (a crucial element in optoelectronics) would be much easier to realize [3].

The defect assignment of particular photoluminescence bands in GaN is still a matter of debate. Our results contribute to the discussion on hypothetical assignments to the V_N, cf. Refs. [5,6], and the defect nature of samples prepared using different techniques and conditions.

The detailed mechanisms of processes characterized by certain spectroscopic signatures, although discussed briefly, are not the primary subject of our Letter. Many such data can be explained by the defect donor and acceptor levels, which we calculated as the corresponding vertical ionization potentials. Indeed, these levels match directly optical absorption data, corrected for the position of the Fermi level (or energy). In the absence of such spectroscopic evidence and without a detailed study of alternative processes, we can only correlate our results with those observed, e.g., in photoluminescence experiments, and if the emission time is short compared to the relevant atomic relaxation time, as we stated, the computed levels could be exploited.

We stress that the mechanism illustrated in Fig. 1 of Ref. [5] assumes a two-particle, electron-hole recombination mediated by phonon relaxation. For a V_N, the mechanism we propose is consistent with this picture, where emission occurs from a relaxed initial state at ~3.46 eV but is more akin to a photoabsorption process. The holes released on photoexcitation, at the VBM or spontaneously ionized from a photoexcited acceptor, could recombine with electrons at a neutral or negatively charged V_N (with their levels in the band gap).

Going beyond the simple two-particle picture, the plausible processes would involve band-to-defect transitions in a many-particle system. For example, when interpreting the lines assigned to acceptors, we suggest that free electrons, at the conduction band minimum (CBM), which are available in photoexcited intrinsic n-type GaN, will recombine with holes, free or trapped at an acceptor. On excitation at the acceptor sites, electrons end up above the Fermi level (e.g., by >0.3 eV when using a helium-cadmium laser [7]), which is above the CBM in the majority of GaN samples, and thermally relax down in energy, which would slow down the process of recombination, but would also probably result in dissociation of the exciton. The electrons at the CBM, in contrast, are available for recombination. An initial process of photoexcitation may stimulate a fast recombination in a three-particle system with the recombining third electron originating from the CBM and in the vicinity of the defect, which would explain the singlet transitions [Fig. 3(a) of Ref. [1]]. We, however, postulate this process; a thorough investigation is required to provide a definitive explanation. Our assertion is that our calculated levels are consistent with the mechanism described and, indeed, correlate with relevant experimental measurements. Furthermore, in a complete analysis, one should also consider the hole (or two holes in the positively charged center) "hopping" between neighboring nitrogens around the impurities, where the atomic configuration rapidly changes.

Our calculations therefore support the acceptor nature of the 3.46 eV band in Mg-doped GaN. We note, however, that at least three signals at about 3.46 eV were identified experimentally [7]. One candidate for assignment based on our calculations is the V_N, as discussed above, which would explain the signal seen in differently prepared and doped samples.

Finally, the statement in Ref. [5] that low-level Mg doping would result in p-type GaN is contradicted by the vast literature on the subject, as it is routinely seen that doping densities of over 10^{19} cm^{-3} are required for significant p-type activation [2]. Detection of holes by magnetic measurements is commonly mistaken for p-type behavior. When a hole is trapped, it does not contribute to the current. The clear absence of such behavior in low-doped samples is the challenge we addressed with our simulations, which in our view have provided the first coherent explanation of the effects of low-level divalent metal doping in the material.

We acknowledge funding from EPSRC Grants No. EP/I01330X/1 and No. EP/K016288/1. This work has been enabled by membership of the UK's HPC Materials Chemistry Consortium (EPSRC Grant No. EP/L000202).

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Received 21 May 2015; published 8 July 2015
DOI: 10.1103/PhysRevLett.115.029702
PACS numbers: 71.55.Eq, 61.72.J-, 78.55.Cr

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[1] J. Buckeridge, C. R. A. Catlow, D. O. Scanlon, T. W. Keal, P. Sherwood, M. Miskufova, A. Walsh, S. M. Woodley, and A. A. Sokol, Phys. Rev. Lett. **114**, 016405 (2015).

[2] H. Amano, in *III-Nitride Based Light Emitting Diodes and Applications*, edited by T.-Y. Seong *et al.* (Springer, Dordrecht, 2013), Chap. 1, p. 1.

[3] H. Morkoç, in *Handbook of Nitride Semiconductors and Devices* (Wiley-VCH, Weinheim, 2009), Vol. 1, Chap. 4, p. 817.

[4] E. R. Glaser, W. E. Carlos, G. C. B. Braga, J. A. Freitas, Jr., W. J. Moore, B. V. Shanabrook, R. L. Henry, A. E. Wickenden, D. D. Koleske, H. Obloh, P. Kozodoy, S. P. DenBaars, and U. K. Mishra, Phys. Rev. B **65**, 085312 (2002).

[5] D. O. Demchenko and M. A. Reshchikov, preceding Comment, Phys. Rev. Lett. **115**, 029701 (2015).

[6] M. A. Reshchikov, D. O. Demchenko, J. D. McNamara, S. Fernández-Garrido, and R. Calarco, Phys. Rev. B **90**, 035207 (2014).

[7] M. A. Reshchikov and H. Morkoç, J. Appl. Phys. **97**, 061301 (2005).